EPR Detection of Aliphatic Disulfide Anion Radicals in Fluid Solution

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Photolysis of alkylthiols (RSH) in EtOH/EtOK in the presence of Bu^tOOBu^t yields the disulfide radical anions $RSSR^{\bullet -}$ in conditions suitable for EPR detection in solution over a wide temperature range.

Anion radicals of disulfides ($RSSR^{\bullet -}$) are believed to play a role in biological processes involving the thiol function, as well as in the biochemistry of radiation protection exerted by aminothiols such as cysteine.[1–5] For these reasons many EPR studies have been carried out on these intermediates in the solid state or frozen solutions: they are usually observed as a result of low temperature radiation exposure (using either X-ray[2] or ^{60}Co γ-radiation[3,4]) of thiols or other sulfur-containing derivatives. Disulfide anion radicals do not seem, however, to have been observed in fluid solution, probably because a general chemical method for their production is not available. Attempts to prepare them by alkali metal reduction of the parent disulfides did not yield the expected EPR signals. To the best of our knowledge the only EPR solution spectra so far reported are those of a five- and of a six-membered cyclic disulfide radical obtained by Gilbert *et al.*[6] by reacting the appropriate dithiols, *i.e.* $HS(CH_2)_3SH$ and $HS(CH_2)_4SH$, with Ti^{III}/H_2O_2 at room temperature in aqueous solutions (pH 5) while flowing through the cavity of the spectrometer.

We wish to report here a reaction which, without the need for a flow system, allowed us to obtain aliphatic disulfide anion radicals in conditions suitable for EPR investigations over a wide temperature range in organic solvents. Solutions of alkylthiols (RSH) in 1 mol dm^{-3} EtOH/EtOK in the presence of Bu^tOOBu^t (0.05, 0.5 and 0.05 cm^3 respectively) were introduced into quartz tubes which were subsequently sealed *in vacuo*. When submitted to photolysis by means of a 500 W high pressure mercury lamp within the cavity of an EPR spectrometer, they yielded the radical anions $RSSR^{\bullet -}$ in a temperature interval ranging between −60 °C and +20 °C. Even lower temperatures can be reached by further addition to these solutions of a certain amount of cyclopropane. The EPR spectra of these radicals disappear when the radiation is shut off. In Table 1 the *g*-factors, a_H values and spectral multiplicity are reported for the cases R = Me (**1**), Et (**2**), Pr^i (**3**) and Bu^t (**4**). At any temperature the lifetime of radical **4** is very short (a few minutes) even under continuous photolysis. On the other hand the radicals **1**–**3** can be observed for at least one hour under steady state conditions at low temperatures, whereas they decay more rapidly at room temperature. The cyclic radicals reported by Gilbert *et al.*[6] can also be obtained with the present reaction, starting from the same compounds. A typical EPR spectrum (a septet with the expected binomial intensity distribution) is shown in Fig. 1 for the case of $CH_3SSCH_3^{\bullet -}$ (**1**).

Table 1 Spectral parameters for the EPR spectra of disulfide radical anions **1–4** obtained at −50 °C from alkyl thiols RSH (R = Me, Et, Pr^i, Bu^t respectively)

Radical	a_H/G	Multiplicity	*g*-Factor
$MeSSMe^{\bullet -}$	5.25	septet	2.0134
$EtSSEt^{\bullet -}$	6.0	quintet	2.0133
$Pr^iSSPr^{i\bullet -}$	5.25	triplet	2.0126
$Bu^tSSBu^{t\bullet -}$	—	singlet	2.0134

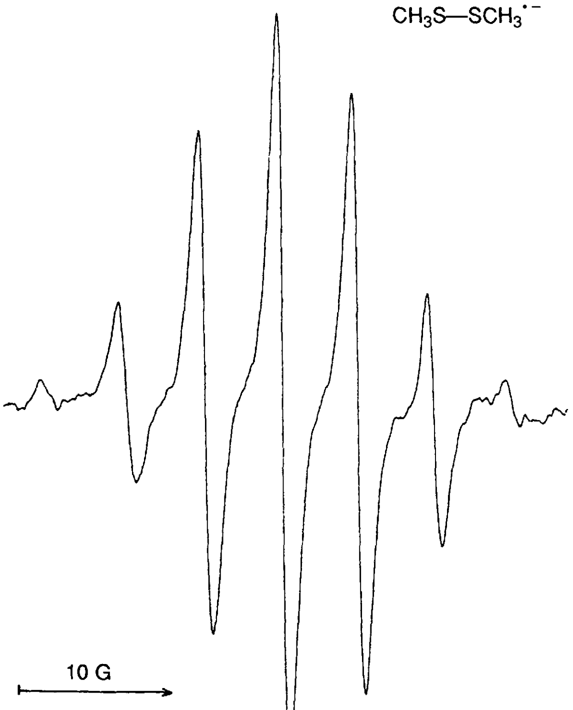

Fig. 1 EPR spectrum of dimethyldisulfide anion radical ($CH_3SSCH_3^{\bullet -}$, **1**) obtained at −50 °C

The same reaction, carried out on thiols in which the carbon alpha to the sulfur is bonded to a conjugated moiety, (*e.g.* $ArCH_2SH$) does not yield the disulfide anion, but the corresponding thioaldehyde anion radical (*viz.* $ArCHS^{\bullet -}$).[7,8] If the aliphatic thiols RSH are completely transformed into their salts RS^-K^+ (thus eliminating all RSH from the equilibrium) the reaction again yields the corresponding thioaldehyde radical anions,[9] rather than the aliphatic disulfide radical anions. The latter observation prompted us to suggest that the mechanism of the present reaction is, probably that described in Scheme 1.[10]

$$
\begin{gathered}
Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \\
Bu^tO^\bullet + RSH \longrightarrow Bu^tOH + RS^\bullet \\
EtO^- + RSH \rightleftharpoons EtOH + RS^- \\
RS^- + RS^\bullet \rightleftharpoons RSSR^{\bullet -}
\end{gathered}
$$

Scheme 1

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Further work is in progress to explore all the implications of this new method of producing disulfide radical anions in solution.

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