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Muonium Containing Thiyl Radicals: $R_2C(\text{Mu})-S^{\bullet}$

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Sulphur centred radicals of the type $R_2C(\text{Mu})-S^{\bullet}$ have been observed by the μSR technique, during the irradiation of a number of thiocarbonyl compounds with positive muons; such thiyl radicals, RS^{\bullet} , have never been detected by e.s.r. spectroscopy in the liquid phase.




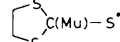
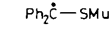
We have recently observed a number of adducts of the light hydrogen isotope, muonium, with carbonyl compounds¹ by the transverse-field μSR technique. These adducts are $R_2\text{COMu}$ radicals, in which the muonium atom is bonded to the oxygen carbonyl atom. Corresponding proton derived radicals, $R_2\dot{\text{C}}\text{OH}$, are well known, and comparisons of the data reveal interesting isotope effects. A logical extension of this work was a study of $\text{C}=\text{S}$ adducts, which were expected to be of the type $R_2\dot{\text{C}}\text{SMu}$. This aim was realised for thiobenzophenone in diethyl ether, which gave a radical with a small [7 G ($G = 10^{-4} \text{ T}$)] coupling constant, as expected for the sulphur bonded adduct, $\text{Ph}_2\dot{\text{C}}\text{SMu}$. This coupling showed a positive temperature dependence, implying that its sign was positive, as with the carbonyl adducts studied in this way.¹

However, extension to an aliphatic series of thiocarbonyl compounds gave results which are in complete contrast with this, since each compound gave rise to a single radical with a large muon hyperfine coupling of ca. 50 G (reduced value, see Table 1), with no precession signals in the low frequency region as observed in the case of $\text{Ph}_2\dot{\text{C}}\text{S}$. We interpret these results in terms of effective muonium addition to the carbon atom of the $\text{C}=\text{S}$ group, giving $R_2\text{C}(\text{Mu})\dot{\text{S}}$ radicals. If this is correct, it is the first observation of thiyl radicals, $R-S^{\bullet}$, in the liquid phase by any magnetic resonance technique. The e.s.r. spectra for RS^{\bullet} radicals in solids are characterised by large g -shifts^{2,3} and it has been suggested that radicals of the type $R-S^{\bullet}$ should be undetectable in solution by e.s.r. spectroscopy because of extensive line broadening arising from the near degeneracy of the SOMO,³ as appears to be the case for alkoxyl radicals, $R-O^{\bullet}$.⁴ Such near degeneracy is responsible for the highly anisotropic g -tensor, and for efficient relaxation of the unpaired electron. This should result in extreme

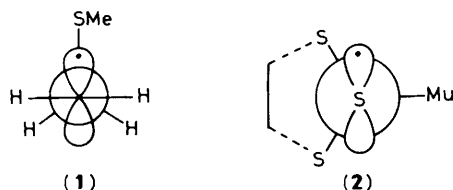
broadening of the e.s.r. lines and of the μSR lines, since T_1 relaxation corresponds to 'interconversion' of the two lines which characterise a muonated radical in its high-field limit. Thus we would not have expected to observe RS^{\bullet} radicals by μSR unless the potential degeneracy is strongly lifted.

We therefore needed to invoke a mechanism by which this orbital degeneracy could be lifted. One possibility was delocalisation of the unpaired electron (as evidenced by the large muon hyperfine couplings) which would raise the energy of the SOMO with respect to the other sulphur π -level. (For

Table 1. Muon coupling constants in a series of muonium adducts of thiocarbonyl compounds.

Radical	A'_μ/G^a	T/K
	55.3 54.8	291 313
	49.8	293
	51.9	293
	39.6 39.3	293 311
	7.66 7.74	273 298

^a These are reduced coupling constants derived from the experimental values by dividing by 3.184. This gives values which are directly comparable with proton hyperfine coupling constants.



solid solutions in protic solvents, hydrogen bonding can lift the degeneracy,³ but this is impossible in the fluid solutions used herein.)

There was a marked reduction in the coupling for the ethylene trithiocarbonate adduct (39.3 G) compared with those of the other radicals listed in Table 1. This is reminiscent of results for alkyl radicals β -substituted with sulphur substituents, such as $\text{MeSCH}_2\text{CH}_2$, in which low β -proton couplings are observed. This is interpreted in terms of a preference for conformation (1) in which the MeS group eclipses the carbon 2p orbital.⁵ One explanation for this is that hyperconjugation⁶ involving the C-S bond is more effective than for the β -C-H bonds in these alkyl radicals. The positive temperature dependences of these β -proton couplings show that the increased weighting of conformations such as (1) has reduced the $a(\beta\text{-H})$ couplings below the free-rotation average. In contrast, for the ethylene trithiocarbonate adduct, the temperature dependence is negative. Thus, although the muon coupling is reduced from that found in the other C=S adducts, presumably because of an increased weighting of β -C-S eclipsed forms such as (2), this preference does not dominate the SOMO of the $(\text{RS})_2\text{C}(\text{Mu})\text{-S}^*$ radical, in which the muon

coupling is still greater than the free-rotation limit. We suggest that while hyperconjugation involving the β -sulphur substituents is important in these thiyl radicals, it is less effective than that for C-Mu bonds. If this order ($\text{C-H} < \text{C-SR} < \text{C-Mu}$) is correct, it nicely supports the suggestion that C-Mu hyperconjugation is more extensive than C-H hyperconjugation.⁷

The combined radical stabilising effect of the two phenyl groups in $\text{Ph}_2\text{C-SMu}$ is presumably sufficient to direct addition to the sulphur atom, rather than to carbon.

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