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Comparison of Proton Hyperfine Coupling Constants for the Monomer and Dimer Radical Cations of Dimethyl Sulphide and Dimethyl Selenide

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Summary The finding that ^{1}H coupling constants for Me_2S^+ and Me_2Se^+ exceed those for the corresponding dimer radical cations $Me_2S\dot{-}SMe_2^+$ and $Me_2Se\dot{-}SeMe_2^+$ by a factor of three in each case is attributed to the antibonding character of the σ^* semi-occupied molecular orbital in the dimeric species.

MONOMER radical cations of Me_2S and Me_2Se have not hitherto been detected by e.s.r. spectroscopy because of their tendency to combine with their counterpart neutral molecules to form the dimer radical cations $Me_2S\dot{-}SMe_2^+$[1–3] and $Me_2Se\dot{-}SeMe_2^+$.[4] This dimerisation can be avoided, however, by using a γ-irradiation technique which generates the monomer radical cations by positive charge transfer to the parent molecules dispersed in a Freon matrix,[5] and here we report the e.s.r. parameters of Me_2S^+ and Me_2Se^+.

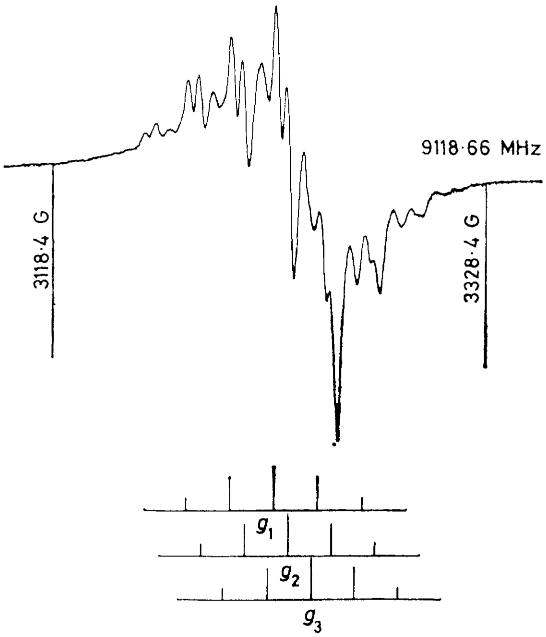

FIGURE. First-derivative e.s.r. spectrum of a γ-irradiated (dose, 1 Mrad) solid solution of 5 mol % dimethyl sulphide in trichlorofluoromethane at 124 K. The spectrum showed a slight orientation dependence at this temperature indicating that the sample was partially ordered. In the spectrum shown here, the three sets of hyperfine components indicated by the stick diagram are more clearly resolved than in the spectrum of a randomly oriented sample.

The e.s.r. spectrum shown in the Figure can be analysed into three sets of hyperfine components with different g factors, each set consisting of a seven-line pattern with a binomial intensity distribution. This analysis† is just what would be expected for the powder spectrum of Me_2S^+, the hyperfine coupling to the six equivalent β-hydrogens being almost isotropic whereas the g-tensor possesses significant anisotropy. The e.s.r. spectrum of Me_2Se^+ showed a much larger g anisotropy but otherwise the analysis was similar and the ^{1}H hyperfine coupling was again extracted from the constant spacings between recurring line positions within each set of hyperfine components. The ^{1}H couplings for these two monomer radical cations are summarized in Table 1 along with the data for the corresponding dimer radical cations.

TABLE 1. E.s.r. parameters for $Me_2M\dot{-}MMe_2{}^+$ and Me_2M^+ ($M = S,Se$) radicals.

Radical	^{1}H Hyperfine coupling/G	g factor
Me_2S^+	$A_{iso} = 20{\cdot}4$ (6H)[a]	$g_1 = 2{\cdot}0233$[a] $g_2 = 2{\cdot}0088$[a] $g_3 = 2{\cdot}0019$[a] $g_{iso} = 2{\cdot}0113$[a]
$Me_2S\dot{-}SMe_2^+$	$A_{iso} = 6{\cdot}8$ (12H)[b] $A_{iso} = 6{\cdot}3$ (12H)[c]	$g_{iso} = 2{\cdot}0103$[b] $g_{iso} = 2{\cdot}0102$[c]
Me_2Se^+	$A_{iso} = 15{\cdot}6$ (6H)[a]	
$Me_2Se\dot{-}SeMe_2^+$	$A_{iso} = 4{\cdot}9$ (12H)[d]	

[a] This work. [b] Ref. 2. [c] Ref. 3. [d] Ref. 4.

The results in Table 1 show that for both the sulphur and selenium radical cations, the ^{1}H coupling constant for the monomer species is about a factor of three greater than that for the dimer species. Assuming that the spin population is shared between the S or Se orbitals in going from monomer to dimer without any significant change of orbital hybridization,‡ a ratio of two would be expected if the ^{1}H couplings in the methyl groups were determined only by the local spin densities in the orbitals of the adjacent S or Se atom.

A contrasting effect is revealed by a comparison of the hyperfine data for the MMe_3 and $Me_3M{\cdot}MMe_3^+$ ($M = Si, Ge$) radicals in Table 2. Here, the ratio of ^{1}H couplings for the monomer and dimer species is only *ca.* 1·1, the average values being 1·14 for silicon and 1·05 for germanium.

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† A similar analysis applies to the powder e.s.r. spectrum of Me_2O^+: J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, in the press.

‡ The 3s character per S atom in the SOMO of $(Bu^tSEt)_2^+$ is *ca.* 6% and about twice that for $Bu^t_2S^+$ (ref. 3). This comparatively small change in orbital hybridization at the heavy atom should have little effect on the interaction between the alkyl group and the unpaired electron in the heavy atom orbitals.

TABLE 2. E.s.r. parameters for $\mathrm{Me_3M}$ and $\mathrm{Me_3M{\cdot}MMe_3^+}$ (M = Si,Ge) radicals.

Radical	^{1}H Hyperfine coupling/G	g factor
$\mathrm{Me_3Si}$	$A_{\mathrm{iso}} = 6{\cdot}28$ (9H)^a	
	$A_{\mathrm{iso}} = 6{\cdot}42$ (9H)^b	$g_{\mathrm{iso}} = 2{\cdot}0031^b$
$\mathrm{Me_3Si{\cdot}SiMe_3^{+}}$	$A_{\perp} = 5{\cdot}55$ (18H)^c	$g_{\perp} = 2{\cdot}0077^c$
	$A = 5{\cdot}65$ (18H)^d	
$\mathrm{Me_3Ge}$	$A_{\mathrm{iso}} = 5{\cdot}5$ (9H)^b	$g_{\mathrm{iso}} = 2{\cdot}0104^b$
	$A_{\mathrm{iso}} = 5{\cdot}28$ (9H)^e	$g_{\mathrm{iso}} = 2{\cdot}0101^e$
	$A_{\mathrm{iso}} = 5{\cdot}31$ (9H)^f	$g_{\mathrm{iso}} = 2{\cdot}0103^f$
$\mathrm{Me_3Ge{\cdot}GeMe_3^{+}}$	$A_{\parallel} = 5{\cdot}39$ (18H)^c	$g_{\parallel} = 2{\cdot}0023^c$
	$A_{\perp} = 5{\cdot}18$ (18H)^c	$g_{\perp} = 2{\cdot}0441^c$
	$A_{\mathrm{iso}} = 5{\cdot}25$ (18H)^c	$g_{\mathrm{iso}} = 2{\cdot}0302^c$

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Again, a ratio of two would have been expected on the basis of the above considerations.§ It is clear, therefore, that some other factor must be involved.

It is proposed that the admixture of a methyl group orbital into the heavy atom orbitals of a dimeric radical species is determined by the character of the MO formed between the heavy atoms. If this MO is antibonding, the methyl group admixture coefficients into the two heavy atom orbitals will have opposite signs resulting in considerable cancellation and a much lower spin density at the methyl hydrogens than half the value for the monomeric species. On the other hand, for a bonding MO the coefficients will reinforce each other resulting in a much larger spin density at the methyl hydrogens than half the value for the monomer radical species. Since the SOMO in $\mathrm{Me_2S\dot{-}SMe_2^{+}}$ is σ^* antibonding whilst that in $\mathrm{Me_3Si{\cdot}SiMe_3^{+}}$ is σ bonding, the results are clearly in accord with this proposal. It should be noted that a comparable argument for π radicals was used by Whiffen[6] many years ago to explain the unexpectedly large proton hyperfine couplings for the $>\mathrm{CH_2}$ group in the cyclohexadienyl radical.

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§ The $\mathrm{SiMe_3}$ and $\mathrm{GeMe_3}$ radicals have pyramidal geometries and should therefore have orbital hybridization ratios similar to those in hexamethyldisilane and hexamethyldigermane.

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