Unstable Intermediates. Part CLXIII.[1] Methyl Radical Anion Adducts: Radiation Effects on Dimethyl Sulphoxide, Dimethyl Sulphone, and their Solutions in Water and Methanol

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Exposure of pure dimethyl sulphoxide to ^{60}Co γ-rays at 77 K gave no detectable e.s.r. features for methyl radicals, but solutions of $(CH_3)_2SO$ in $(CD_3)_2SO$ gave methyl radicals with normal e.s.r. parameters. In contrast, as shown by Chung *et al.*, $\dot{C}D_3$ radicals in this medium have an abnormally low ^{2}H hyperfine coupling (2.99 G) which is taken as evidence for 'adduct' formation ($\dot{C}D_3 \cdots SOCD_3^-$). Both sulphoxides in methanol gave normal methyl radicals ($\dot{C}H_3$ and $\dot{C}D_3$), but in neutral and alkaline aqueous glasses $\dot{C}H_3$ and $\dot{C}D_3$ radicals formed as adducts. Dimethyl sulphone gave abnormal methyl radicals in the pure state, and both normal and abnormal methyl radicals in methanolic solutions. A ^{33}S hyperfine coupling of 22 G was detected for these adducts $[\cdot\dot{C}H_3 \cdots S(O)_2CH_3^-]$. A previously unidentified radical in irradiated trimethylphosphine oxide, having $a(CH_3)$ *ca.* 20 and $a(^{31}P)$ *ca.* 72 G is identified as the adduct $H_3C\cdot \cdots :P(O)(CH_3)_2^-$. A variety of other radicals were detected in irradiated dimethyl sulphoxide and its solutions, including $Me\dot{S}O$, $Me_2\dot{S}O^+$, and the dimer cation $Me_2S(O){-}S(O)Me_2^+$. The parent anion, $Me_2\dot{S}O_2^-$, has been identified as a primary product in irradiated dimethyl sulphone.

SINCE the discovery of a residual weak interaction between methyl radicals and bromide ions following dissociative electron capture (1) there have been several

$$CH_3Br + e \longrightarrow \dot{C}H_3 \cdots Br^- \qquad (1)$$

species, which we describe here as 'anion-adducts'.[2-8] We concluded previously[3] that these species, $R \cdots X^-$, are not properly described as the radical anions, RX^-, but are genuine alkyl radicals which, formed in a solid-state 'cavity', are unable to leave the site of the anions X^- and exhibit a weak charge-transfer interaction which does not modify their shape or reactivity appreciably, but only their e.s.r. spectra.[3] Thus the ^{13}C hyperfine coupling in $H_3{}^{13}C \cdots Br^-$ is quite normal for planar methyl radicals,[6] and, despite a contrary suggestion,[9] the reactivity of $\cdot CH_3$ in methyl cyanide is more a function of the crystal structure than the presence of a weak interaction with cyanide ions.[6] It is not necessary for the leaving group to be anionic, although this will generally be the case, and an example in which the leaving group is neutral has been described.[8] We feel that this is likely to prove to be a phenomenon of wide occurrence in solid-state studies, though probably not in liquid-phase e.s.r. spectroscopy, and failure to recognise the phenomenon may lead to misassignments.[4] One possible example is the recent detection of a radical exhibiting a small hyperfine coupling to bromine which was identified as the β-bromo-radical, $(CH_3)_2\dot{C}CH_2Br$,[10] but which we think is more likely to be the adduct $(CH_3)_3C\cdot \cdots Br^-$.[11]

All these results are for dissociative electron-capture processes. There is some analogy between this type of 'anion-adduct' and the weak spin–spin interaction sometimes detected between pairs of radicals trapped in solids. These are usually formed by bond homolysis.[12] It is less likely to occur for electron-loss centres, a possible exception being methyl radicals in irradiated alkali-metal acetates.[13] The isotropic proton hyperfine

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[6] E. D. Sprague, K. Takeda, J. T. Wang, and F. Williams, *Canad. J. Chem.*, 1974, **52**, 2840.

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[13] S. Kubota, M. Iwaizumi, and T. Isobe, *Chem. Phys. Letters*, 1974, **25**, 247.

coupling was found to increase steadily from 21.8 G for the lithium salt to a normal ' free ' value of 23.3 G for the caesium salt. The explanation offered involved hindered rotation, but it is possible that, after loss of an electron, there is a very weak residual bonding between methyl and the ejected carbon dioxide molecule [reactions (2) and (3)] the extent of interaction being governed

$$CH_3CO_2^- \longrightarrow CH_3CO_2 + e \qquad (2)$$

$$CH_3CO_2 \longrightarrow {\cdot}CH_3 \cdots CO_2 \qquad (3)$$

by the space available for separation within the parent site.

Dimethyl sulphoxide has not been extensively studied by radiation chemists. The most significant solid-state work is that of Williams and his co-workers, who showed that electron capture leads to the formation of methyl radicals which, in the case of $\cdot CD_3$ from $(CD_3)_2SO$ are weakly complexed with the anion $(CD_3)SO^-$ [reaction (4)].[7] They also detected CH_3SO radicals in irradiated single crystals.[14] In contrast, pulse radiolysis optical studies reveal that solvated electrons are a major direct product both for aqueous solutions[15] and the pure liquid.[16-18] For e_{aq}, a relatively slow reaction with dimethyl sulphoxide (k 1.7×10^6 l mol^{-1} s^{-1})[15] gave a species with an absorption maximum at 350 nm, which was described as the anion, $(CH_3)_2SO^-$, but this was not detected in the pure compound. Instead, a transient species absorbing at 600 nm was obtained, which is either the parent radical-cation, $(CH_3)_2SO^+$ or some radical derived therefrom.[16] Two other species absorbing in the 260—350 nm region were not positively identified.[18]

$$(CD_3)_2SO + e \longrightarrow D_3C\cdot \cdots S(O)CD_3^- \qquad (4)$$

The aim of the present work was to learn more about $\cdot CD_3$ and $\cdot CH_3$ adduct formation in dimethyl sulphoxide and to see if there was any tendency for adduct formation in the related dimethyl sulphone molecule. We also hoped to be able to detect the parent anions $(CH_3)_2SO^-$ and $(CH_3)_2SO_2^-$ by low-temperature studies.

EXPERIMENTAL

Dimethyl sulphoxide, dimethyl sulphone, and their perdeuteriated analogues were the purest grades available and were used directly. Water was doubly distilled, and D_2O and CD_3OD were *ca.* 99% deuteriated.

Samples were irradiated as small spherical glassy beads in a Vickrad ^{60}Co γ-ray source at a dose rate of 1.7 Mrad h^{-1} for up to 2 h. Solutions in 6M sulphuric acid were prepared by adding the substrate dropwise into the acid at 0 °C with rapid stirring and cooling to 77 K directly after dissolution.

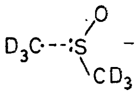
E.s.r. spectra were measured with a Varian E3 spectrometer at 77 K directly after exposure. Samples were annealed in the insert Dewar flask after decanting the liquid nitrogen, and were re-cooled to 77 K whenever significant changes were observed in the continuously monitored e.s.r. spectra. Q-Band spectra were measured on a superheterodyne spectrometer constructed in these laboratories by Mr. J. A. Brivati.

RESULTS AND DISCUSSION

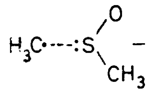
Anion-adducts.—Our results for pure $(CD_3)_2SO$ confirm those previously described.[7] The ^2H isotropic coupling of 2.97 G is appreciably less than that normally found for $\cdot CD_3$ radicals in the solid state (*ca.* 3.58 G). As stressed by Chung *et al.*,[7] $(CH_3)_2SO$ irradiated at 77 K does not contain trapped methyl radicals, so that reaction (5) occurred at 77 K for the protio-compound.

$$\cdot CH_3 + (CH_3)_2SO \longrightarrow CH_4 + H_2\dot{C}S(O)CH_3 \qquad (5)$$

We therefore studied dilute solutions of $(CH_3)_2SO$ in $(CD_3)_2SO$. Surprisingly, this gave clearly detectable methyl radical features (Figure 1a) which exhibit no evidence of adduct formation. This result shows the remarkable subtlety of the phenomenon, in that (I) is stable at 77 K but (II) is not. In previous studies, both $\cdot CH_3$ and $\cdot CD_3$ have formed adducts, so the significant difference between (I) and (II) may lie in the difference between the anions, at least in part. This result shows that loss of $\cdot CH_3$ in $(CH_3)_2SO$ is largely due to the greater reactivity of the C–H over the C–D bond.[19]



(I)



(II)

During the annealing process, just prior to the irreversible loss of $\cdot CD_3$, the hyperfine coupling increased from the value for the adduct (2.95 G) to that for the free species (3.5 G) (Figure 1b). This behaviour parallels that observed for the halide ion adducts, and is another clear indication of the weakness of the bond involved.

We have been unable to detect any clear features for adducts containing ^{33}S [^{33}S, 0.74% abundant, has I 3/2]. However, several of the Q-band spectra showed a group of lines on the high-field side of the main $\cdot CD_3$ adduct features that could well be the $M_I - 3/2$ feature. If so, $A(^{33}S) \approx 13$ G and is fairly isotropic (Figure 1c).

Solutions of $(CH_3)_2SO$ or $(CD_3)_2SO$ in CD_3OD gave ' normal ' $\cdot CH_3$ and $\cdot CD_3$ radicals, as found for alkyl bromides.[3] This effect, which was thought to be due to increased solvation of the ejected anions, again shows how subtle the phenomenon must be.

In contrast, both forms of dimethyl sulphoxide gave adduct methyl radicals in aqueous and aqueous alkaline glasses (D_2O–8M-NaOD) (see Table 1). The contrast with methanolic solutions is so surprising that we have sought an explanation other than a medium effect. In view of the results of Gilbert *et al.*,[20] who found that hydroxyl radicals from the titanous ion and hydrogen

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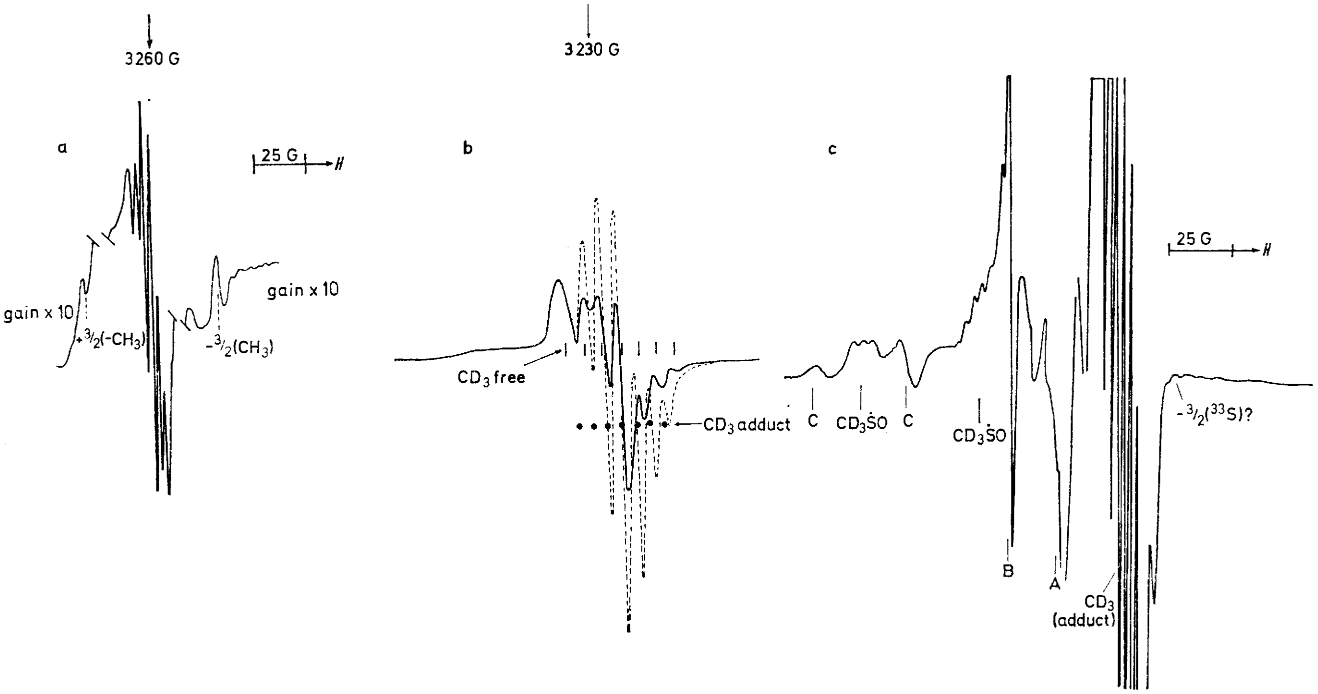


FIGURE 1 First derivative e.s.r. spectra for dimethyl sulphoxide after exposure to ^{60}Co γ-rays at 77 K: a, at X-band for $(CD_3)_2SO$ containing 20% $(CH_3)_2SO$, showing features for the $\cdot CD_3$ adduct and free $\cdot CH_3$ radicals; b, at X-band for $(CD_3)_2SO$, showing the change from $\cdot CD_3$ adduct to free $\cdot CD_3$ on annealing; and c, at Q-band, for $(CD_3)_2SO$, showing features for $\cdot CD_3$ adducts and centres A—C

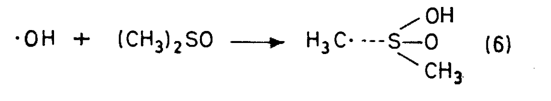
TABLE 1

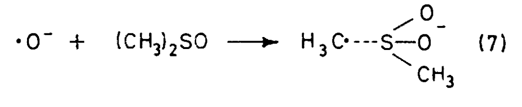
E.s.r. parameters for various methyl radical adducts

		Hyperfine coupling (G) [a]				
			Other nuclei			
Adduct	System	Protons		$A_{\parallel}$	$A_{\perp}$	A_{iso}
$CH_3 \cdots Br^-$ [b]	CH_3Br	20.6		56.7 [b]		
$CH_3 \cdots Br^-$ [c]	CH_3Br	21.0	(^{81}Br)	58.3	±28.3	38.3 or 0.57
$CH_3 \cdots I^-$ [c]	CH_3I	21.0	(^{127}I)	78	±56	63.3 or −11.3
$CH_3 \cdots CN^-$ [d]	CH_3CN	22.3	(^{13}C)			3.4
$CD_3 \cdots SOCD_3^-$ [e]	$(CD_3)_2SO$	(^{2}H) 2.99				
$CD_3 \cdots SOCD_3^-$ [f]	$(CD_3)_2SO$	(^{2}H) 2.97	(^{33}S)	*ca.* 13		
$CH_3 \cdots SO_2CH_3$ [f]	$(CH_3)_2SO_2$	20.8	(^{33}S)	*ca.* 22		
	$+D_2O$	21.0	(^{33}S)	*ca.* 22		
	$+CH_3OD$	20.5	(^{33}S)	*ca.* 23		
$CH_3 \cdots PO(CH_3^-)_2$ [f]	$(CH_3)_3PO$	20 ± 1	(^{31}P)	*ca.* 72		

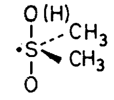
[a] G = 10^{-4} T. [b] Ref. 2. [c] Ref. 3. [d] Ref. 6. [e] Ref. 7. [f] This work.

peroxide system add to dimethyl sulphoxide to give methyl radicals, we suggest that the adduct methyl radicals were formed by process (6) or (7). This is


$$\cdot OH + (CH_3)_2SO \longrightarrow H_3C\cdots S(OH)(=O)CH_3 \quad (6)$$


$$\cdot O^- + (CH_3)_2SO \longrightarrow H_3C\cdots S(O^-)(=O)CH_3 \quad (7)$$

supported by our results for dimethyl sulphone (see below). [Reaction (6) was discussed by Gilbert *et al.* in terms of an alkoxyl-like radical written as $(CH_3)_2S(OH)\dot{O}$. We consider that the hydroxyl radical adduct is more likely to have a structure (III) analogous to phosphoranyl radicals, but we are not convinced that this is a necessary intermediate in the formation of methyl (see below)]. In contrast, free $\cdot CH_3$ and $\cdot CD_3$ radicals were formed in 6M-sulphuric acid glasses, so that here electron capture seems to dominate.



(III)

Irradiated dimethyl sulphone gave clear evidence for methyl-adduct formation (Table 1). The value for

$a(^1H)$ is similar to that found for methyl radical adducts in aqueous dimethyl sulphoxide glasses, which supports the postulate that these are formed by reaction (6) rather than by direct electron capture. On annealing, we were unable to detect the formation of ' free ' $\cdot CH_3$ or $\cdot CD_3$ radicals prior to their irreversible loss.

In these cases, well-defined features for adducts containing ^{33}S were detected (Figure 2a), giving an almost isotropic coupling of *ca.* 22 G.

Solutions of $(CH_3)_2SO_2$ in CD_3OD gave two sets of methyl-radical features (Figure 2b), one of which is due to normal methyl and the other to the anion adduct. On annealing further, the ' normal ' radicals were lost before the adduct radicals, in contrast with the behaviour of the bromide ion adducts, and that from $(CD_3)_2SO$ which gave ' normal ' alkyl radicals on annealing.[2,3]

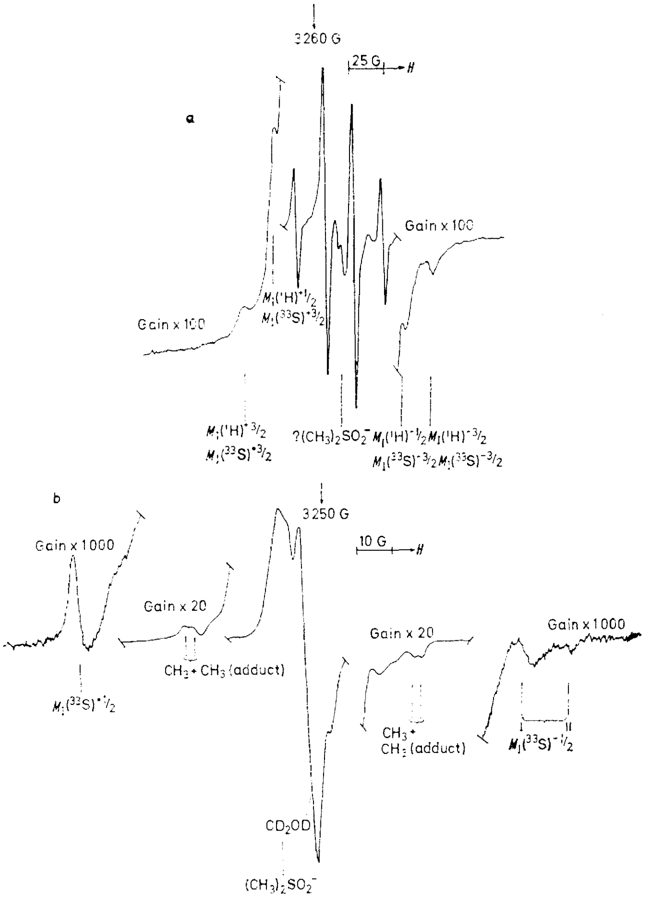
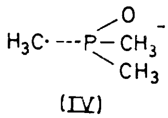


FIGURE 2 First derivative X-band e.s.r. spectra for dimethyl sulphone after exposure to ^{60}Co γ-rays at 77 K: a, showing features for the methyl radical adduct and some ^{33}S satellite lines; and b in CD_3OD, showing features for two types of methyl radicals and for the radical anion $[(CH_3)_2SO_2]^-$, including ^{33}S features

Solutions in water and aqueous alkali gave the same adducts but, curiously, the methyl radicals formed in 6M-sulphuric acid glasses were ' free '. We suggest that this effect is caused by protonation of the ejected anion by neighbouring H_3O^+ of HSO_4^- ions, with consequent loss of the weak ' adduct ' bond.

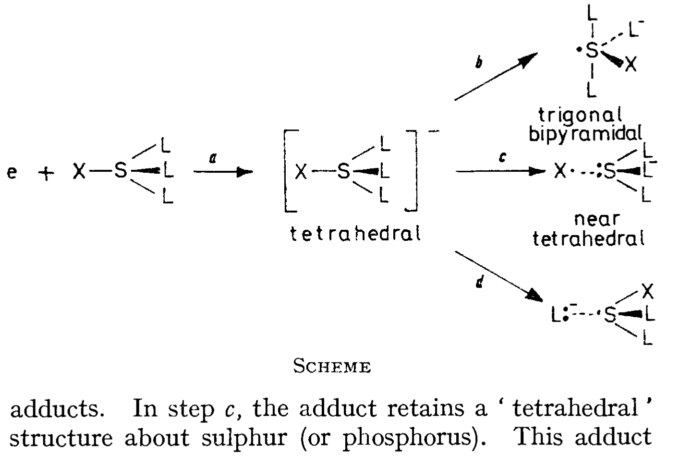
In view of these results, we returned to some of our results for alkyl-phosphorus radicals to see if similar adduct formation ever occurred since hyperfine coupling to ^{31}P should be well defined. This has enabled us to interpret a previous unassigned spectrum in irradiated trimethylphosphine oxide.[21] This spectrum is clearly a doublet of quartets, and must be due to the methyl radical adduct (IV) with $A(^1H)$ *ca.* 20 and $A(^{31}P)$ *ca.* 72 G.


$H_3C\cdot\cdots P(O)(CH_3)_2^-$

(IV)

(See Figure 1b of ref. 20 for a typical e.s.r. spectrum.) There is some anisotropy in the phosphorus coupling, but this is poorly defined and small. This suggests that the interaction is with the *s–p* hybridised ' lone-pair ' electrons on phosphorus. The coupling of 72 G, corresponding to *ca.* 2.0% 3*s* character on phosphorus, suggests slight spin delocalisation, in accord with the reduced proton coupling. This result can be compared with the value of 2.25% 3*s* character for the $\cdot CH_3\cdots SO_2CH_3^-$ adduct described above. The large isotropic and small anisotropic coupling accords with the proposed structure, in which the *s–p* hybridised orbital of the ejected anion which originally contributed to the σ-bond is primarily involved in the interaction.

Adducts of this type are formed, in our view, as a result of bond stretching which is halted by repulsive environmental forces prior to complete separation. The residual bond strength must be small, and may be zero or even negative, but hyperfine interaction with the diamagnetic anion is diagnostic. It can be argued for the sulphur and phosphorus compounds that since the parent radical anions are stable species, this bond stretching should either not occur, or should be reversed when the fragments are unable to escape. This, however, is not a necessary conclusion (Scheme). Initial electron addition *a* must lead to a vibrationally excited anion. This may relax in a variety of ways, one of which (*b*) involves bond-bending, to give a stable anion-radical, but others (*c* and *d*) involve bond stretching to give adducts. In step *c*, the adduct retains a ' tetrahedral ' structure about sulphur (or phosphorus). This adduct



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[21] A. Begum and M. C. R. Symons, *J.C.S. Faraday II*, 1973, 43.

can only change to the stable anion in *b* by re-making the X · · · S bond and simultaneously moving from the ' tetrahedral ' to the trigonal bipyramidal configuration. There will undoubtedly be a considerable barrier to such a change, which therefore need not occur at 77 K. Process *d*, which is commonly observed in phosphorus radical chemistry, may also give rise to adducts, but these have not yet been detected. In this case, the radical $\cdot SL_2X$ will have a somewhat flattened pyramidal structure, so that again a considerable change in shape must occur before reversion to the radical-anion can occur.

Other Radicals.—Dimethyl sulphoxide. The task of identifying the species responsible for the range of e.s.r. features obtained in this study is more difficult than that in our related studies of organophosphorus radicals,[21-24] since it is rarely possible to detect features from radicals containing ^{33}S, and those from ^{32}S tend to bunch together in the *g* 2 region. Some gain was achieved by using a Q-band spectrometer (Figure 1c) since several species absorbed at a variety of *g* values, but still, absence of information from sulphur nuclei makes identification difficult.

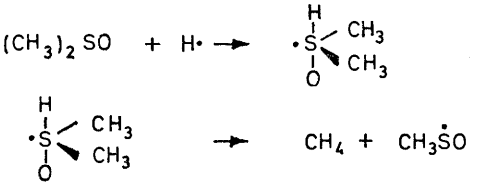
The best defined centre is the $CH_3\dot{S}O$ radical previously identified by Nishikida and Williams.[14] Their data are given in Table 2 together with our own. This centre is thermally stable and can therefore be studied free of other centres after annealing. We have been unable to detect ^{33}S features in the powder spectra, but these were well defined in the single crystal studies.[14] Our value for g_1 is somewhat smaller than that reported previously: we have checked our value at Q-band frequencies and it seems to be correct. Our powder spectra show the same change in the apparent proton hyperfine coupling as observed by Nishikida and Williams.[14] This was explained in terms of a restricted rotation such that only two equivalent protons couple at low temperatures, but free rotation sets in on warming to give three equivalent protons. The ^{33}S tensor components show unambiguously that this is a π-radical, similar to the phosphinyl radicals studied previously.[25] The related radical SO_2^- is well known,[26,27] but the dialkyl radicals $R_2S^{+\cdot}$ are less well defined, possible because of their tendency to ' dimerize ' to give $(R_2S\text{–}SR_2)^+$ cations.[28,29]

There are two reasonable modes of formation for CH_3SO, electron return [(8)—(10)] or, alternatively, *via*

$$(CH_3)_2SO \longrightarrow (CH_3)_2SO^+ + e \qquad (8)$$

$$(CH_3)_2SO^+ + e \longrightarrow [(CH_3)_2SO]^* \qquad (9)$$

$$[(CH_3)_2SO]^* \longrightarrow \cdot CH_3 + CH_3\dot{S}O \qquad (10)$$



(11)

(12)

hydrogen atom attack [(11) and (12)]. The excited state, $[(CH_3)_2SO]^*$, which may also be formed directly by interaction with high energy electrons, can undergo bond homolysis as in (10). If this were a major route, however, one might expect to detect ' free ' methyl radicals together with the adducts. However, if (11) and (12) represent the correct pathway, evidence for $H\cdot_t$ might be expected. No evidence for such centres was obtained. Our Q-band spectra at 77 K suggest that $CH_3\dot{S}O$ radicals are a relatively minor primary component, rather than being a secondary product formed on annealing. Its marked stability on annealing may be related to the stability exhibited by $\cdot SO_2^-$ radicals.[26]

Of the other centres formed in the pure compounds, species A (Table 2) has a strong multi-component feature at *g* 2.007, only clearly evident in the Q-band spectra (Figure 1c). At least six components were resolved, separated by *ca.* 2.0 G, for the perdeuteriated compound.

TABLE 2

E.s.r. parameters for various radicals in irradiated dimethyl sulphoxide and dimethyl sulphone

			Hyperfine coupling (G)				*g* Values		
Radical	System		A_1	A_2	A_3	A_{iso}	g_1	g_2	g_3
$CH_3\dot{S}O$ [a]	$(CH_3)_2SO$	(^1H)				11.6	2.023	2.011	2.003
		(^{33}S)	−14	−21	+59	+8			
$CD_3\dot{S}O$ [b]	$(CD_3)_2SO$	(^2H)				*ca.* 2.0	2.021	2.012	2.003
$(CD_3)_2\dot{S}O^+$ [b]	$(CD_3)_2SO$	(^2H)				*ca.* 2.0		*ca.* 2.007	
$(CH_3)_2\dot{S}O^+$ [b]	$(CH_3)_2SO\text{–}D_2SO_4$	(^1H)				12.0			
$[(CH_3)_2SO]_2^+$	$(CH_3)_2SO\text{–}D_2SO_4$	(^1H)				*ca.* 3.0	*ca.* 2.01	2.01	2.001
$(CH_2)_2\dot{S}O^+$	$(CH_3)_2SO\text{–}CD_3OD$	(^1H)				12.0	2.008	2.008	2.002
		(^{33}S)	83	*ca.* 38	*ca.* 38	*ca.* 53			
$(CH_3)_2\dot{S}O_2$	$(CH_3)_2SO_2$					*ca.* 3			
$(CH_3)_2\dot{S}O_2$	$(CH_3)_2SO_2\text{–}D_2SO_4$					*ca.* 3	2.016	2.011	2.003
$(CH_3)_2\dot{S}O_2$	$(CH_3)_2SO_2\text{–}CD_3OD$	(^{33}S)	143	122	122	129	2.012	2.012	2.003
$H_2\dot{C}SO(CH_3)$	$(CH_3)_2SO\text{–}NaOD$	(^1H)	−25	−17.5	−17.5	−20.0		2.003	
$H_2\dot{C}SO_2(CH_3)$	$(CH_3)_2SO_2\text{–}CD_3OD$	(^1H)	−26	−17	−17	−20.0		2.003	

[a] Ref 14 [b] This work

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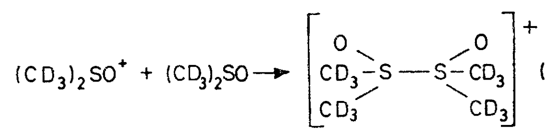
[28] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[29] M. C. R. Symons, *J.C.S. Perkin II*, 1974, 1618.

[Unfortunately, clearly assignable features for this radical were never obtained from pure $(CH_3)_2SO$.] Since this centre was rapidly lost on annealing, and since a broad feature having $g_\perp$ 2.01 grew in at about the same temperature, we tentatively identify A as the parent cation, $(CD_2)_2\dot{S}O^+$ (see below). This radical, which is related to the well known $\dot{S}O_3^-$ radical anion,[30] and to the radical $CH_3\dot{S}O_2$,[20] is expected to react with the parent material to give the dimer cation [reaction (13)]. It is isoelectronic with the radical $(CH_3)_2\dot{P}O$, detected in irradiated trimethylphosphine.[21] This radical, which was well characterised by its ^{31}P hyperfine components, had $a(^1H)$ 5.6 G at temperatures well above 77 K, but restricted rotation effects caused the M_I ±2 and ±1 components to broaden on cooling, so that only a triplet of features was detected. Both the sulphur and phosphorus centred radicals are expected to be pyramidal,[31] but on going from phosphorus to sulphur there should be a flattening, as observed, for example, for the series $R_3Al^{-\cdot}$, $R_3Si\cdot$, and $R_3P^{+\cdot}$.[32] This will move the methyl groups apart and facilitate rotation. It will also cause the proton hyperfine coupling to become more negative as the radical becomes flatter. If the coupling for $(CH_3)_2\dot{P}O$ is positive then that for $(CH_3)_2\dot{S}O^+$ should be smaller, which is not the case. It may be that the coupling for $(CH_3)_2\dot{P}O$ is -5.6 G in which case a (calculated) coupling to ^1H of *ca.* -12 G is possible.

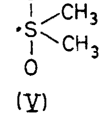


(13)

Species B, a strong singlet in the g 2.01 region, is thought to be the dimer shown in equation (13). This species is better defined in other systems and is discussed below.

Species C has g_1 2.025, g_2 2.019, and probably g_3 in the free-spin region. No hyperfine coupling was detectable. It could possibly be the parent anion $[(CH_3)_2\dot{S}O]^-$, but in the absence of detectable ^{33}S coupling there is nothing to support this suggestion. It was not detected in aqueous solutions which are thought to give the parent anions in the liquid phase.[16]

Indeed, no features clearly assignable to $[(CH_3)_2SO]^-$ were obtained from neutral, alkaline, or acidic aqueous glasses. Nor were we able to identify the ·OH radical adduct (V) with any certainty, despite the expectation that it could be an intermediate in the formation of the methyl radical adduct. Clear features for ·OH(·OD) radicals were obtained from neutral glasses and O^- features and SO_4^- and SO_3^- features were obtained from the alkaline and acidic glasses respectively. For the neutral glasses features for $H_2\dot{C}S(O)CH_3$ radicals were obtained, and these were very strong for the alkaline glasses (Figure 3). We suggest that in the latter, the parent anions are present [equilibrium (14)] and that



(V)

$$OH^- + (CH_3)_2SO \rightleftharpoons H_2O + \bar{H}_2\ddot{C}SOCH_3 \quad (14)$$

these lose electrons in the primary process to give $H_2\dot{C}SOCH$ directly. The magnitude of the anisotropic ^1H coupling for this species suggests that delocalisation onto sulphur is of no great significance despite the presence of a 'lone-pair' of electrons on the sulphur atom.

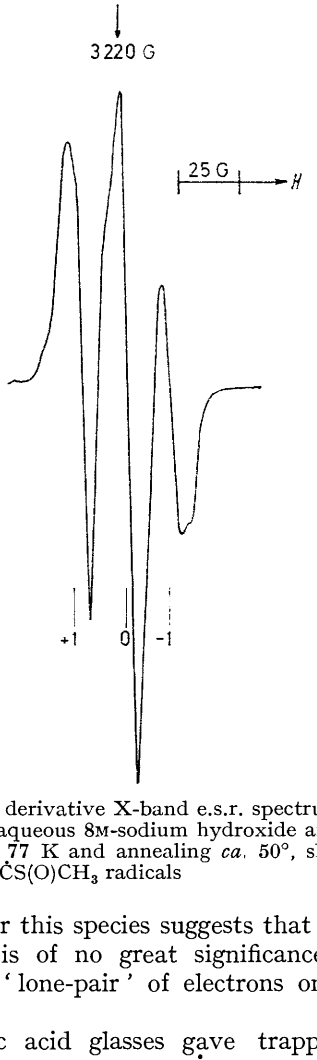


FIGURE 3 First derivative X-band e.s.r. spectrum for dimethyl sulphoxide in aqueous 8M-sodium hydroxide after exposure to ^{60}Co γ-rays at 77 K and annealing *ca.* 50°, showing features assigned to $H_2\dot{C}S(O)CH_3$ radicals

6M-Sulphuric acid glasses gave trapped hydrogen atoms (or ·D) together with $CH_3\dot{S}O$ radicals and probably $(CH_3)_2\dot{S}O^+$ radicals (Figure 4a). The high yield of $CH_3\dot{S}O$ radicals suggests that processes (11) and (12) are significant for this medium, but no features for the hydrogen atom adducts were detectable. When concentrated solutions were annealed for a prolonged period all signals except that shown in Figure 4b were lost. This centre comprises a group of *ca.* 13 lines with g_{av} *ca.* 2.006 and $a(^1H)$ *ca.* 3.0 G. We suggest that this is the dimer

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[30] G. W. Chantry, A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1962, **5**, 233.

[31] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[32] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290.

cation depicted in equation (13). This is isostructural with the ' dimers ', $R_3P{-}PR_3^+$ often detected in irradiated phosphorus(III) compounds which exhibit large, nearly isotropic hyperfine coupling to two equivalent ^{31}P nuclei.[33,34] A search for possible ^{33}S features which should have twice the normal relative intensity because of the presence of two equivalent sulphur atoms was defeated by the high noise levels.

The species thought to be $(CH_3)_2\dot{S}O^+$ has a set of lines separated by *ca.* 12 G (Figure 4a) but these are partially hidden by features from $\cdot SO_3^-$, $\cdot SO_4^-$, and $CH_3\dot{S}O$, so a proper analysis is not possible. The proton coupling of *ca.* 12 G agrees with the ^2H coupling of *ca.* 2.0 G from the species thought to be $(CD_3)_2\dot{S}O^+$ and with the results for methanolic solutions discussed below.

Solutions in methanol (CD_3OD in most experiments) gave high yields of e_t^-, so that dry electron capture by dimethyl sulphoxide is not an efficient process. The central region gives evidence for $\dot{C}D_2OD$ radicals in addition to the free $\cdot CH_3$ or $\cdot CD_3$ radicals. The only other well defined species (D) had particularly clear parallel ^{33}S features, which appeared as 12 G multiplets for $(CH_3)_2SO$ solutions (Figure 5). Corresponding perpendicular features were not clear, probably because the symmetry is not axial, but if two inflections are taken as the M_I ±3/2 ' perpendicular ' features, the data in Table 2 are obtained. A possible assignment is to the $CH_3\dot{S}O$ radical, but the differences between these parameters and those previously reported (Table 2) are surely too large. The increase in $A_{\parallel}$ (^{33}S) from 59 to 83 G could possibly be a consequence of a libration or hindered rotation giving partial averaging in the former case, but then we would expect a temperature dependence in the g and $A(^{33}S)$ parameters for the radical in pure dimethyl sulphoxide which was not detected. The differences are far too large to be simply a medium effect. We favour the assignment to the radical $(CH_3)_2\dot{S}O^+$ discussed above. A proton coupling of *ca.* 12 G is reasonable, in which case, since there are at least five features in the parallel components, we conclude that the methyl groups are freely rotating as implied above.

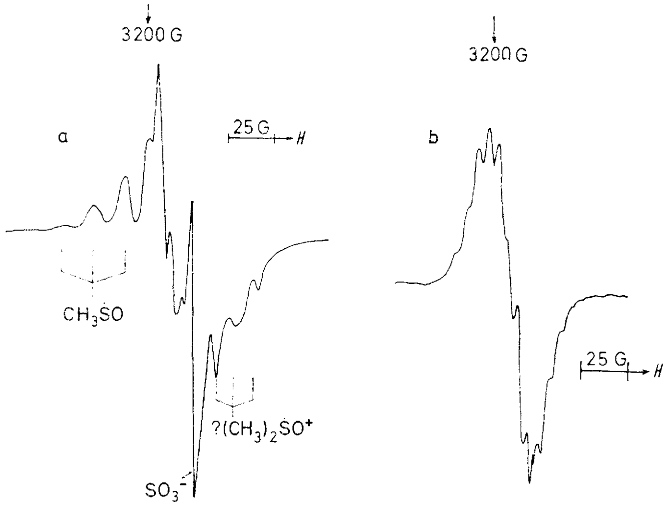


FIGURE 4 First derivative X-band e.s.r. spectra for dimethyl sulphoxide in 6M-D_2SO_4 after exposure to ^{60}Co γ-rays at 77 K: a, after slight annealing, showing features assigned to $CH_3\dot{S}O$ and $[(CH_3)_2SO]^+$ radicals and b, during the annealing process, showing features assigned to $[(CH_3)_2SO]_2^+$

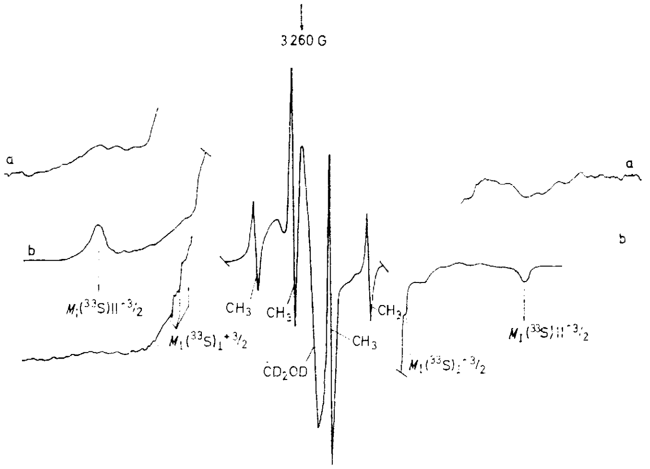
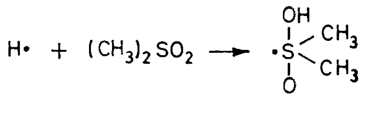


FIGURE 5 First derivative X-band e.s.r. spectrum for dimethyl sulphoxide in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, showing free CH_3 radicals and, at high gain, wing lines assigned to $^{33}\dot{S}O(CH_3)_2^+$, (a), and $^{33}\dot{S}O(CD_3)_2^+$, b

If we take $A_{\perp}$ as +38 G then we find A_{iso} 53 and $2B$ 30 G, whence $a_{3s}^2 = 0.054$ and $a_{3p}^2 = 0.54$ using the atomic parameters recommended elsewhere.[31] The total spin density is reasonable for $(CH_3)_2\dot{S}O^+$. The $3p:3s$ ratio is large, but certainly possible for $(CH_3)_2\dot{S}O^+$, and we therefore favour this assignment.

Other Radicals from Dimethyl Sulphone.—At 77 K, a multicomponent g 2 feature with $a(^1H)$ *ca.* 3 G could be the primary anion, which is expected to have structure (III) (without the hydroxy-proton). Corresponding phosphoranyl radicals have $a(CH_3)$ *ca.* 2.5 G,[35] but we were unable to detect ^{33}S satellite lines if they were present because of the high noise level. On annealing, a triplet assigned to $H_2\dot{C}S(O)_2CH_3$ grew in. No clear features for the primary electron-loss centres were observed.

Solutions in water gave the methyl radical adducts and $\cdot OH$ ($\cdot OD$) radicals, together with $H_2\dot{C}S(O)_2CH_3$ radicals on annealing. Solutions in sulphuric acid gave a species having g_1 2.016, g_2 2.011, and g_3 *ca.* 2.003 and substructure with a *ca.* 3 ± 1 G. This is thought to be the parent anion, or, in view of the modified g tensor components, the protonated form, possibly from hydrogen atom attack [reactions (15)].



$$H\cdot + (CH_3)_2SO_2 \longrightarrow \cdot\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{|}}{S}}\begin{matrix} CH_3 \\ CH_3 \end{matrix} \qquad (15)$$

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[33] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1589.

[34] T. Gillbro, C. M. L. Kerr, and F. Williams, *Mol. Phys.*, 1974, **28**, 1225.

[35] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

Again, solutions in CD_3OD gave multicomponent features with $d_\perp$ 2.012 and $g_\parallel$ *ca.* 2.003 (this feature is hidden by those for $\dot{C}D_2OD$). In this case we were able to detect ^{33}S satellite lines (Figure 2b) which gave $A_\parallel$ (^{33}S) 143 and $A_\perp$ (^{33}S) 122 G. From these we find

(VI)

A_{iso} 129 and $2B$ 14 G, on the assumption that both values are positive. This gives a^2_{3s} *ca.* 0.13 and a^2_{3p} *ca.* 0.25. The latter value corresponds reasonably to the a^2_{3p} values obtained for similar phosphoranyl radicals. The value for a^2_{3s} is appreciably less than that for the structurally similar phosphoranyl radicals (VI).[35] This undoubtedly reflects, in part, the change from OR to O^- ligands. It may also result from the change from phosphorus to sulphur, which is expected to favour delocalization onto the ligands in the antibonding orbital involved.

Conclusions.—Our major conclusion is that dissociative electron capture will frequently generate anion adducts, but that the bonding is extremely weak in most cases. It seems that the parent cations $(CH_3)_2\dot{S}O^+$ have been detected and that they readily react to give $\underset{\cdot}{[}(CH_3)_2SO]_2^+$ ' dimers '. No good evidence for $[(CH_3)_2\dot{S}O]^-$ anions has been forthcoming. However, $[(CH_3)_2\dot{S}O_2]^-$ anions have been detected and have a structure similar to those for analogous phosphoranyl radicals.

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