Unstable Intermediates. Part 167.[1] Electron Spin Resonance Studies of Trifluorosilyl and Related Radicals

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Exposure of SiF_4 to ^{60}Co γ-rays at 77 K gives a species (A) exhibiting strong hyperfine coupling to ^{29}Si and to three ^{19}F nuclei, together with weak coupling to four other equivalent ^{19}F nuclei. This species is tentatively identified as $SiF_3^{\bullet}$ interacting weakly with a neighbouring SiF_4 molecule, but other possibilities are discussed. Species very similar to A, but with different sub-structures, are obtained from Si_2F_6 and SiF_3H, together with $SiF_2H^{\bullet}$ in the latter case. Species A is not obtained from $O(SiF_3)_2$ or $SiF_3(NMe_2)$, but species similar to A containing two strongly coupled ^{19}F nuclei have been detected. These are identified as $F_2\dot{S}iOSiF_3$ and $\dot{S}iF_2(NMe_2)$ respectively. The radical $\dot{O}(SiF_3)$ is obtained in certain samples of SiF_4.

THE first silyl radical to be studied by e.s.r. spectroscopy was $SiH_3^{\bullet}$, formed by γ-irradiation of SiH_4 in an argon matrix at 4.2 K.[2] The small magnitude of the proton hyperfine coupling (7.6 G) * led me to suggest that the radical is pyramidal,[3] and this has been confirmed by the observation of a large hyperfine coupling to ^{29}Si.[4,5] However, Gordy and his co-workers[4] postulated a nearly 'tetrahedral' configuration for $SiH_3^{\bullet}$, whereas only a minor deviation from planarity was originally deduced.[3] Better defined spectra have more recently been obtained for various alkyl-substituted silyl radicals[6,7] in fluid solution. Such radicals have also been formed in the solid state by radiolysis of suitable methylsilanes,[8] and the results lead to the conclusion that all the silyl radicals, $SiR_3^{\bullet}$, are indeed pyramidal, but the 3*p* to 3*s* ratio of *ca.* 5.7 shows that they are far from being 'tetrahedral.'

Since alkyl radicals, $CR_3^{\bullet}$, are probably planar[9,10] (but *cf.* ref. 11), and $CF_3^{\bullet}$ radicals are strongly pyramidal, with F–C–F angles probably close to 109°,[12,13] it is reasonable to conclude that $SiF_3^{\bullet}$ radicals should have FSiF angles between 90 and 109°. Angles close to 109° were inferred by Milligan *et al.*[14] in their infrared studies of $SiF_3^{\bullet}$ formed by photolysis of SiF_3H in rare-gas matrices at 4.2 K. This result, based on the silicon isotope shift in the vibrational frequencies, shows that the degree of bending is large. This was confirmed by the e.s.r. studies of Merritt and Fessenden,[15] who generated $SiF_3^{\bullet}$ in SF_6 at 77 K by electron irradiation *in situ*. The coupling to ^{29}Si of 498 G corresponds to a 3*s* orbital population of *ca.* 41%, on the basis of a computed coupling of 1 220 G for unit population.[16] Even if the spin-density is strongly confined to silicon this suggests a F–Si–F angle of less than 109°.

Merritt and Fessenden[15] also studied $SiFH_2^{\bullet}$ and $SiF_2H^{\bullet}$ in this medium, the results suggesting that the pyramidal character falls between that for $SiH_3^{\bullet}$ and $SiF_3^{\bullet}$, as expected. The large ^1H coupling of 89.9 G for $SiF_2H^{\bullet}$ is noteworthy, and can be compared with that of 82.5 G for the isoelectronic radical $[PHO_2]^{-\bullet}$.[17] In contrast with these conclusions, the photoelectron (p.e.) spectrum of $PF_3^{\bullet}$ was originally interpreted as showing that $[PF_3]^{+\bullet}$ is planar or nearly so.[18] However, it has now been shown that these results can be satisfactorily accommodated in terms of a pyramidal cation.[19]

Some years ago, Florin *et al.*[20] reported an e.s.r. study of SiF_4 both pure and in a xenon matrix after irradiation at 4.2 K. They obtained an extremely complex spectrum which was interpreted in terms of distorted $SiF_3^{\bullet}$

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* $1\ G = 10^{-4}\ T$.

[1] Part 166, M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, preceding paper.

[2] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *Adv. Chem. Ser.*, 1962, **36**, 50.

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[5] G. S. Jackel and W. Gordy, *Phys. Rev.*, 1968, **176**, 443.

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[13] M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, 1967, **46**, 3193.

[14] D. E. Milligan, M. E. Jacox, and W. A. Guillory, *J. Chem. Phys.*, 1968, **49**, 5330.

[15] M. V. Merritt and R. W. Fessenden, *J. Chem. Phys.*, 1972, **56**, 2353.

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

[17] J. R. Morton, *Mol. Phys.*, 1962, **5**, 217.

[18] J. P. Maier and D. W. Turner, *J.C.S. Faraday II*, 1972, 711.

[19] J. Raferty, W. G. Richards, D. W. Turner, and M. C. R. Symons, unpublished work.

[20] R. E. Florin, D. W. Brown, and L. A. Hall, *J. Phys. Chem.*, 1962, **66**, 2672.

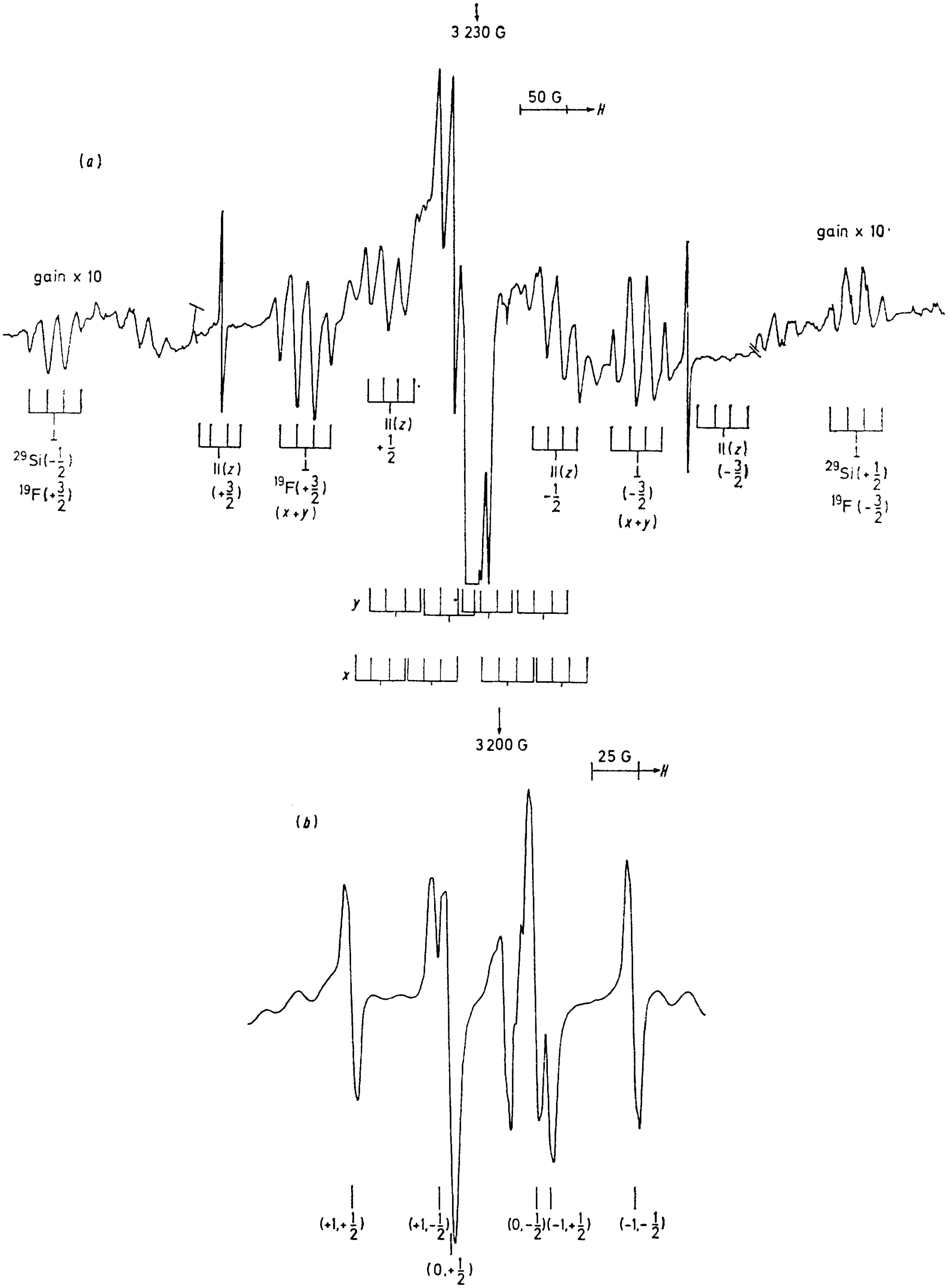

FIGURE 1 First-derivative e.s.r. spectra for SiF$_4$ after exposure to ^{60}C γ-rays at 77 K showing (*a*) features assigned to species A, together with a stick diagram appropriate to SiF$_3$• radicals weakly interacting with a neighbouring molecule, and (*b*) features for species B, thought to be $\dot{O}$(SiF$_3$)

radicals having one ^{19}F nucleus with an isotropic coupling of 176 G and two equivalent ^{19}F nuclei with coupling constants of 100 G. Each feature appeared as quartets of *ca.* 18 G splitting. This was interpreted in terms of a weak interaction with three fluorine nuclei of neighbouring molecules. The radicals were thought to be freely rotating, even at 4.2 K.

The aim of the present work was to study this complex spectrum in greater depth, in the light of the liquid-phase data for SiF_3.[15] A variety of other potential sources of $SiF_3^{\cdot}$ were selected in addition to SiF_4, and in particular Si_2F_6 and $O(SiF_3)_2$ were studied in the expectation that the weak interaction with three fluorine nuclei might involve another SiF_3 group within the radical rather than being an intermolecular phenomenon. After this work was completed, a single-crystal study of irradiated SiF_4 was published.[21] This work is of great help in understanding the present results.

EXPERIMENTAL

Materials.—The compound SiF_4, SiF_4 in xenon (mole fraction *ca.* 0.1), SiF_3H, Si_2F_6, $O(SiF_3)_2$, and $SiF_3(NMe_2)$ were purified materials supplied in evacuated quartz tubes by Dr. I. A. Ellis.

Hyperfine coupling constants for $SiF_3^{\cdot}$ and related radicals

Radical	Matrix	Hyperfine coupling (G) [a]					
		$^{19}F_{\parallel}$	$\perp$	iso	$^{29}Si_{\parallel}$	$\perp$	iso
$SiF_3^{\cdot}$	SF_6 [b]			136.6			−498.0
	SiF_4 [c]	215.2	(80.6, 106.5)	134.1	−561.6	−504.4	−523.4
	SiF_4 (A)	180	117 [d]	138	−562	−501	−521.3
$SiF_2H^{\cdot}$	SF_6 [b]			77.8	(^{1}H) 89.9		
	SiF_3H (C)		*ca.* 75 [e]		(^{1}H) *ca.* 89		
$F_2\dot{Si}OSiF_3$	$O(SiF_3)_2$ (D)	180	125	143.3 [f]	−590	−540	−556.7
$\dot{Si}F_2(NMe_2)$	$SiF_3(NMe_2)$ (E)	175	110	131.7	−395	−345	−361.7
$\dot{O}(SiF_3)$	SiF_4 (B)	F^1 (1)		46.5			
		F^2 (2)		51.5			

[a] *g ca.* 2.004 and almost isotropic for $SiF_3^{\cdot}$. [b] Ref. 15. [c] Ref. 21. [d] Obtained along the symmetry axes. The value of 117 G is based on the outermost features. From the inner features $A_{\parallel}$ = 81 G. [e] Anisotropy was present but not clearly defined. [f] $A_{iso.}$ = 145 G at *ca.* 150 K.

Irradiations.—Samples were irradiated in quartz tubes at 77 K in a Vickrad ^{60}C γ-ray source, at a dose rate of 1.7 Mrad h^{-1}.

E.S.R. Spectroscopy.—E.s.r. spectra were recorded at 77 K on a Varian E3 spectrometer. Samples were annealed in the insert Dewar flasks after decanting the liquid nitrogen and were recooled to 77 K whenever significant changes were noticed in the continuously monitored spectra.

RESULTS AND DISCUSSION

The e.s.r. spectra of irradiated SiF_4 both pure and in xenon solution are similar to those of Florin *et al.*[20] except that ^{29}Si satellites are better defined [Figure 1(*a*)] and yield a reliable perpendicular hyperfine coupling constant (Table). All the lines in this spectrum, apart from the 507 G doublet for hydrogen atoms and the central lines from the quartz tube, are assigned to a single species, A. Annealing resulted in the simultaneous loss of all the features. Thus it is unlikely that more than one paramagnetic species is involved.

Florin *et al.*[20] analysed their e.s.r. spectra in terms of one strongly coupled and two more weakly coupled fluorine nuclei. This certainly gives a reasonable fit, but it ignores the outer 'shoulders,' marked || in Figure 1(*a*), which are too intense to be part of the ^{29}Si satellites. I therefore prefer an analysis based on an axially symmetric coupling as shown in the reconstruction in Figure 1(*a*). Subsidiary splitting was also present in the parallel features, but the coupling was slightly reduced. This difference was maintained in the poorly defined $M_I = \pm\frac{1}{2}$ features. Certain preparations gave a second species (B) after long irradiation [Figure 1(*b*)]. This is thought to be formed from an impurity.

A species very similar to A was obtained from SiF_3H after irradiation at 77 K (Figure 2). The main difference is in the minor splitting, well defined quartets in the outermost ($\pm\frac{3}{2}$) perpendicular features being replaced by poorly defined multiplets containing about six more closely spaced features. Nevertheless, the major parameters are so similar that I feel the species must be the same as A. Additional broad features obscured the spectral region inside the $M_I = \frac{3}{2}$ lines for species A. These are indicated in Figure 2 as species C. They became better defined on warming above 77 K.

Features similar to those for species A were also obtained from irradiated Si_2F_6, although again the multiplet features were somewhat different. It is probable that a second species is responsible for some of the inner features, but these were always too poorly defined because of overlap to warrant any attempt at assignment. They were lost irreversibly on slight annealing. In contrast, $O(SiF_3)_2$ did not give species A, a broad triplet with a subsidiary quartet structure being obtained (Figure 3). Again, relatively well defined ^{29}Si satellites were detected for this species (D), and annealing experiments confirmed that only one type of radical was responsible. Irradiated $SiF_3(NMe_2)$ gave weak features (E) very similar to those for (D) shown in Figure C. In this case, however, an intense central set of lines was obtained, which undoubtedly stems from one or more radical species based on the NMe_2 moiety.

Species A.—In order to explain the curious form of the powder spectrum for irradiated SiF_4 [Figure 1(*a*)] I had originally considered the possibility of radicals such as (I) or (II) formed by electron capture at the possible

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[21] A. Hasegawa, K. Sogabe, and M. Miura, *Mol. Phys.*, 1975, **30**, 1889.

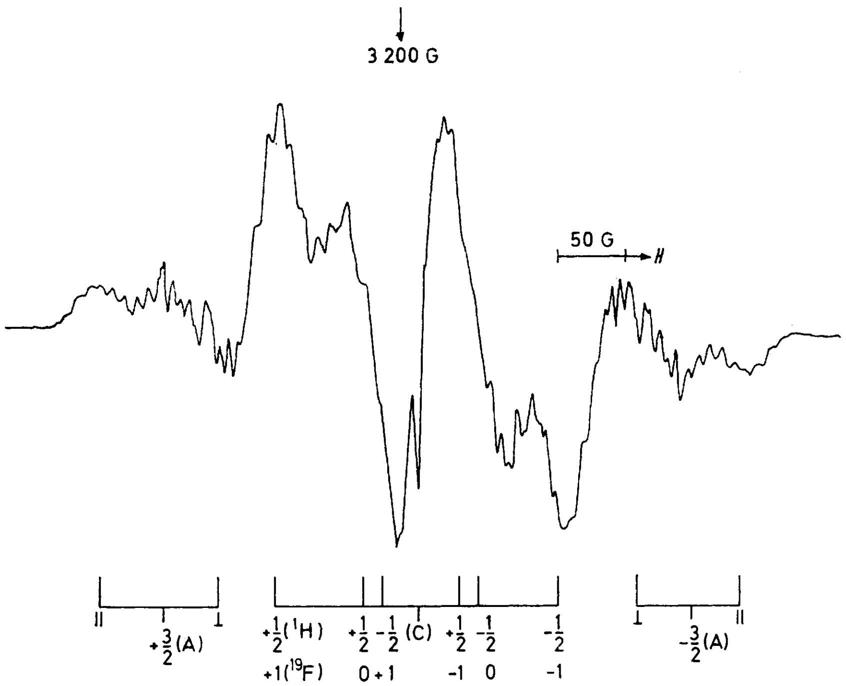


FIGURE 2 First-derivative e.s.r. spectrum for SiF_3H after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to species A ($SiF_3^{\bullet}$) and species C

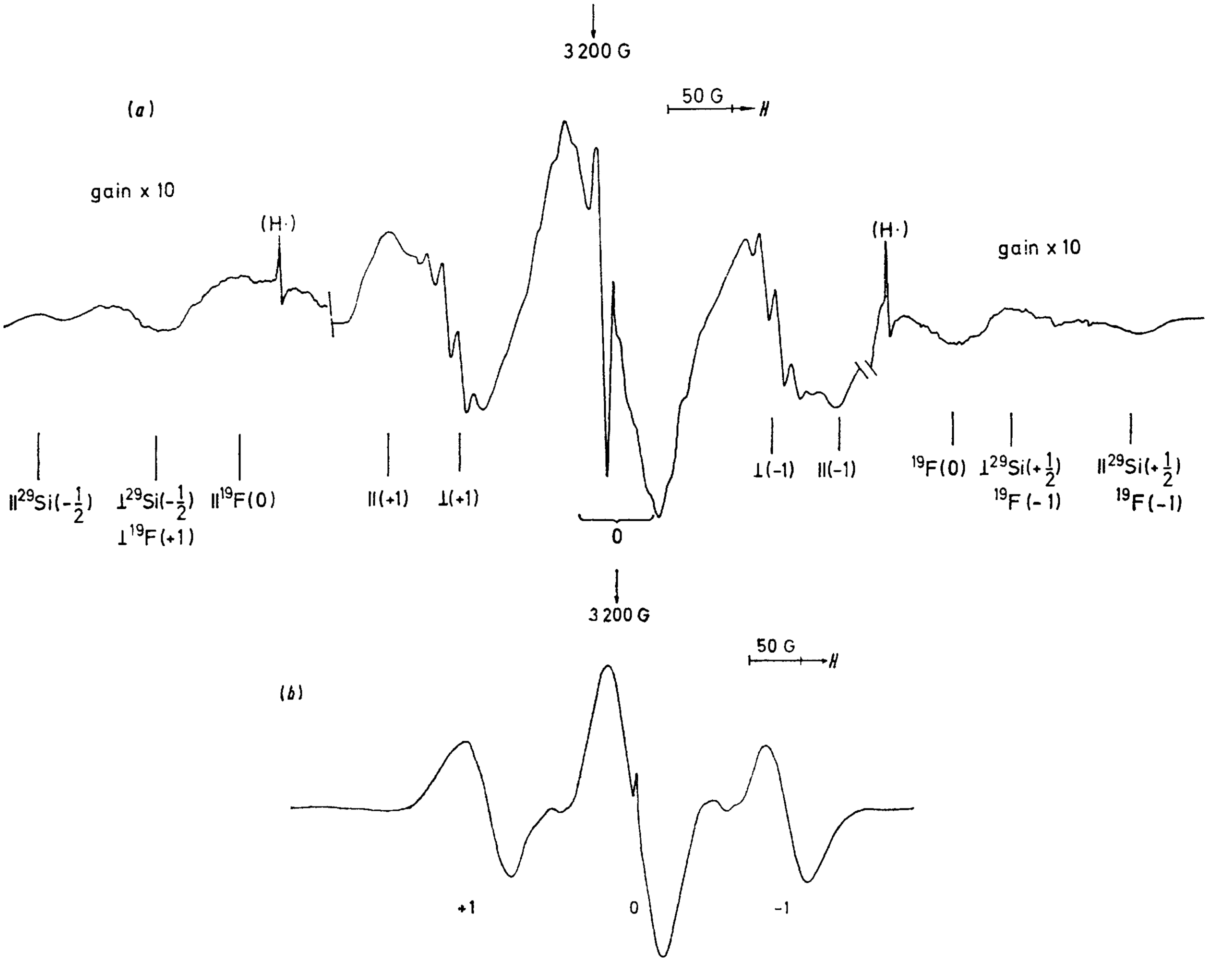
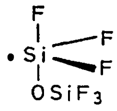
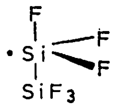


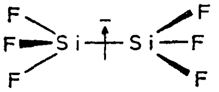
FIGURE 3 First-derivative e.s.r. spectra for $O(SiF_3)_2$ after exposure to ^{60}Co γ-rays at 77 K, showing (*a*) features assigned to $F_2SiOSiF_3$ (D) radicals at 77 K, and (*b*) the same at *ca.* 150 K

impurity centres $F_3SiOSiF_3$ and F_3SiSiF_3. Radical (I) would display a large coupling to one ^{19}F, a smaller coupling to two others, and very small coupling to three

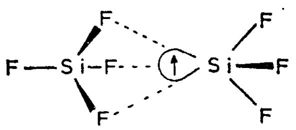

(I)


(II)

more, in good agreement with the quoted results of Florin *et al.*[20] Indeed, even the magnitudes of the coupling to ^{19}F and ^{29}Si are very reasonable for (I). However, pure $F_3SiOSiF_3$ failed to give this species. (This does not disprove the theory because the parent anions were not detected in irradiated $F_3SiOSiF_3$, but could have been formed in an SiF_4 medium.) Irradiation of F_3SiSiF_3 did give the required species, but, in this case, structure (II) is thought to be improbable. By analogy with phosphorus[22] and sulphur[23,24] radicals, the symmetrical structure (III), with the extra electron in the Si–Si σ^* orbital, is more reasonable for the anion.


(III)

It would seem, from the results of Hasegawa *et al.*,[21] that in fact $SiF_3^{\cdot}$ must be the correct formulation for radical A in SiF_4. Thus four sets of magnetically equivalent radicals were formed, implying loss of any one of the four fluorine ligands from SiF_4. The single-crystal spectra showed that there are, in fact, three equivalent fluorine ligands per radical, the isotropic coupling constants being close to those reported by Merritt and Fessenden.[15] Thus the weak interaction with three extra ^{19}F nuclei, so characteristic of these spectra, must be an intermolecular effect as originally supposed.[20] This is most unusual, and a highly specific interaction is required to give such a well defined structure. Hasegawa *et al.*[21] suggested that one ^{19}F from each of the three neighbouring SiF_4 molecules are responsible. I favour interaction with three ^{19}F ligands of a single molecule. Provided the ejected $F^{\cdot}$ or F^- moves away from its original site, the $SiF_3^{\cdot}$ radical could well move slightly towards this vacancy, which would bring it close to a neighbour in the correct orientation to give (IV). {On either theory, the very small coupling (*ca.* 3—4 G) to several further ^{19}F nuclei evident in the single-crystal features and on the present parallel features [Figure 1(*a*)] must stem from coupling to more remote ^{19}F nuclei.} Interaction with one molecule is supported by my results and those of Florin *et al.*[20] for solutions in xenon. The 18 G quartet splitting was not lost, which strongly suggests complexing with one SiF_4 molecule only.


(IV)

I conclude that species A is, indeed, $SiF_3^{\cdot}$ interacting with three ^{19}F nuclei from a neighbouring SiF_4 molecule. The task is, therefore, to reconcile the powder e.s.r. spectrum in Figure 1(*a*) with this assignment.

Interpretation of the E.S.R. spectrum for $SiF_3^{\cdot}$.—The outermost strong features, assigned provisionally to the parallel and perpendicular $M_I = \pm\frac{3}{2}$ features for $^{28}SiF_3^{\cdot}$, are well defined quartets [Figure 1(*a*)]. However, the $M_I = \frac{1}{2}$ features are not apparent. A consideration of the symmetry of the radical $SiF_3^{\cdot}$ shows that this is to be expected, provided the radical is strongly pyramidal, as must be the case. For a field parallel to the symmetry (z) axis the three ligands are magnetically equivalent and should exhibit four hyperfine features with an apparent parallel coupling between the true parallel value and the isotropic value. However, for a field perpendicular to z the three hyperfine coupling constants are never equal (Figure 4). However, two constants are equivalent for a field along two orthogonal axes (x and y). The important result is that for all directions in the xy plane the sum of the three hyperfine couplings is a constant, as shown in Figure 4. This explains why the $M_I = \pm\frac{3}{2}$ 'perpendicular' lines are so intense. For H_x, the small coupling should be equal to the minimum coupling of the true tensor components. My spectra give 81 G which compares well with the single-crystal value of 80.6 G.[21] From this value, and the requirement that the total apparent perpendicular coupling is equal to the separation between the '$M_I = \pm\frac{3}{2}$' features (351 G), the remaining separations for the features predicted from Figure 4 were calculated and are shown in Figure 1(*a*). These predictions agree well with the experimental spectrum.

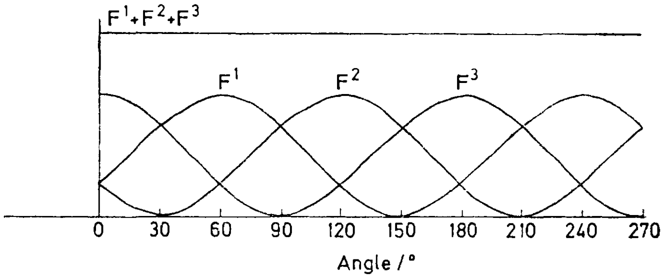


FIGURE 4 Angular variation of the ^{19}F hyperfine coupling for $SiF_3^{\cdot}$ rotating about the symmetry axis

The $M_I = \pm\frac{3}{2}$ 'perpendicular' features are also well defined for $^{29}SiF_3^{\cdot}$ radicals. These should give the true perpendicular component for the coupling to $^{29}Si^{\cdot}$, and the resulting value of 501 G is close to that given by

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

[23] H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Buzinski, *J. Phys. Chem.*, 1970, **74**, 40.

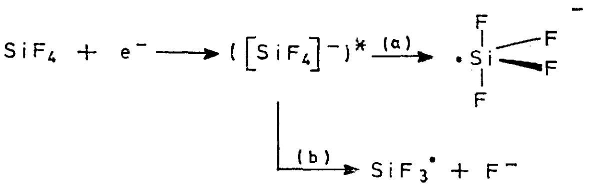
[24] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

Hasegawa *et al.* (504.4 G). Unfortunately, the parallel features for $^{29}SiF_3^{\cdot}$ were too weak to be clearly detected. At high gain and high modulation, shoulders in the correct region were apparent, but without the single-crystal data I would have had no confidence in this result. Again knowing the value for $A_{\parallel}(^{29}Si)$, extra features between the outer sets of perpendicular features can be assigned to the $M_I = \pm\frac{1}{2}$ parallel features for $^{29}SiF_3^{\cdot}$, as indicated in Figure 1(*a*).

Thus the powder spectrum is satisfactorily explained. The most characteristic features are the outer $M_I = \pm\frac{3}{2}$ 'perpendicular' features separated by 351 G and I recommend that these be used as being diagnostic of $SiF_3^{\cdot}$ in a polycrystalline or glassy sample.

The initial damage process for SiF_4 is expected to be as in (1) and (2) but electron return could give excited SiF_4 [equation (3)]. The $[SiF_4]^+$ cation is isoelectronic with $[PO_4]^{2-}$,[25] and is expected to have its unpaired electron confined to one or more fluorine ligands. No such species was detected. Process (2) is thought to represent the normal mode of electron addition to molecules of this type. The anion $[SiF_4]^{-\cdot}$ is isoelectronic with $PF_4^{\cdot}$, which has a well established e.s.r. spectrum.[26] The bond-bending distortion (2a) normally competes with bond stretching, (2b),[27] rather than being a necessary precursor to (2b). In this case (2b) seems to be favoured. Alternatively, electron return may be important.

$$SiF_4 \longrightarrow [SiF_4]^+ + e^- \qquad (1)$$



(2)

$$(SiF_4)^* \longrightarrow SiF_3^{\cdot} + F^{\cdot} \qquad (3)$$

The structural implications of these results for $SiF_3^{\cdot}$ have been discussed by Hasegawa *et al.*[21] The ^{29}Si hyperfine coupling parameters can be converted into approximate 3*s*- and 3*p*-orbital populations by dividing the isotropic and anisotropic values by those computed for unit population.[16] The results are *ca.* 0.43 3*s* and 0.61 3*p* character. This suggests that the extent of delocalisation on to the ligands is small and this agrees with the small coupling constants to ^{19}F. The very low 3*p* : 3*s* ratio surely means that the F–Si–F angle is less than the tetrahedral value. Unfortunately, as stressed by Hasegawa *et al.*,[21] it is unsafe to use the relative directions of the maximum coupling to ^{19}F in the three ligands to derive bond angles because these do not necessarily correspond to the bond directions. Nevertheless, the results do agree with a structure having a bond angle equal to or less than the tetrahedral value.

My results show that $SiF_3^{\cdot}$ is also a major irradiation product of SiF_3H and Si_2F_6. For $SiF_3^{\cdot}$ in Si_2F_6, coupling to three ^{19}F nuclei of *ca.* 18 G was again observed, but for SiF_3H there was a greater number of more closely spaced features. If structures such as (IV) are important this is understandable since a variety of such structures are now possible. For SiF_3H, $SiF_3^{\cdot}$ is probably formed by electron loss [equations (4) and (5)], whereas for Si_2F_6 it is probably formed by dissociative electron capture [equation (6)].

$$SiF_3H \longrightarrow [SiF_3H]^+ + e^- \qquad (4)$$

$$[SiF_3H]^+ \longrightarrow (H^+) + SiF_3^{\cdot} \qquad (5)$$

$$e^- + Si_2F_6 \longrightarrow SiF_3^{\cdot} + [\colon SiF_3]^- \qquad (6)$$

I had hoped to detect the symmetrical anion $[F_3Si\dot{-}SiF_3]^-$ with the extra electron in the Si–Si σ* orbital, but no such species was obtained at 77 K. In this case, the weak secondary coupling to three ^{19}F nuclei could stem from interaction with the ejected anion, but in view of the results for SiF_4 this is clearly not a necessary requirement.

Species B.—The spectrum for this species can be analysed in terms of an isotropic hyperfine coupling to two equivalent fluorine nuclei (52.5 G) and a slightly smaller coupling to a third (46.5 G). The spectrum is isotropic at 77 K, but $g_{av.}$ is greater than the free-spin value (2.0076). A possible identification is the radical $\dot{O}(SiF_3)$, formed by electron and proton loss from the impurity $SiF_3(OH)$. This species is expected to have its unpaired electron largely on oxygen. The *g* values should be >2.0023, with $g_{\parallel} \gg g_{\perp}$. Thus if this identification is correct, the molecule must be rotating. Unfortunately, I was unable to detect any features for radicals containing ^{29}Si nuclei, because of the presence of many other lines of about the predicted intensities. This species can be compared with $PF_2(O_2^{\cdot})$ previously reported, which had $A_{iso.}(^{19}F) = 52.5$ G.[28] Only low concentrations of $SiF_3(OH)$ can have been present in these samples, so the formation of $\dot{O}(SiF_3)$ is indicative of mobility for the primary cation $[SiF_4]^+$, even at 77 K. This probably occurs by electron transfer, which implies that the preferred structure for $[SiF_4]^+$ is not greatly distorted from the tetrahedral structure of SiF_4.

The fact that this radical is rotating whereas $SiF_3^{\cdot}$ is stationary provides support for the concept that $SiF_3^{\cdot}$ is weakly bonded to a neighbouring molecule, as in (IV).

Species C.—This poorly defined species formed in irradiated SiF_3H is thought to be $SiF_2H^{\cdot}$, previously studied in an SF_6 matrix.[15] The derived data are comparable (Table) but, unfortunately, this species annealed before species A so that the expected ^{29}Si satellite features were always completely hidden by more intense lines from species A. The broad lines assigned to $SiF_2H^{\cdot}$ again showed signs of small superhyperfine splitting, which may indicate that there is again a weak coupling to

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[25] S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc.* (*A*), 1970, 1239.

[26] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.

[27] B. W. Fullam and M. C. R. Symons, *J.C.S. Dalton*, 1975, 861.

[28] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1323.

neighbouring molecules. The $SiF_2H^{\cdot}$ radical is presumably formed from $SiF_3H^{\cdot}$ by dissociative electron capture.

Species D.—This species, the major paramagnetic product from $O(SiF_3)_2$, exhibited hyperfine coupling to two equivalent ^{19}F nuclei [Figure 3(*a*)] which became isotropic on annealing [Figure 3(*b*)]. Hence I suggest that D is $F_2\dot{S}iOSiF_3$. In this case, the 10 G minor quartet splitting seen clearly on the ± 1 perpendicular features can be assigned to the three fluorine nuclei in the $O(SiF_3)$ ligand, and there is no need to postulate any intermolecular interaction. The hyperfine parameters are very similar to those for $SiF_3^{\cdot}$ (Table). No electron-loss centre could be detected for $(SiF_3)_2$.

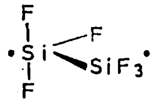
Species E.—This centre, formed in irradiated $SiF_3(NMe_2)$, had an e.s.r. spectrum comparable with that for D, and hence I suggest $SiF_2(NMe_2)^{\cdot}$ as a reasonable structure. The intense central lines are largely due to $H_2\dot{C}N(Me)SiF_3$, with proton and ^{14}N coupling constants similar to those for $H_2\dot{C}NMe_2$ in the solid state.[29] The radicals $[SiF_3(\dot{N}Me_2)]^+$ or $NMe_2^{\cdot}$ do not seem to be present. The radiation-induced reactions are, therefore, probably (7)—(9).

$$SiF_3(NMe_2) \longrightarrow [SiF_3(\dot{N}Me_2)]^+ + e^- \qquad (7)$$

$$[SiF_3(\dot{N}Me_2)]^+ + SiF_3(NMe_2) \longrightarrow H_2\dot{C}N(Me)SiF_3 + [SiF_3(NMe_2H)]^+ \qquad (8)$$

$$SiF_3(NMe_2) + e^- \longrightarrow F^- + \dot{S}iF_2(NMe_2) \qquad (9)$$

Reactions of Si_2F_6.—The primary anion for this molecule, $[Si_2F_6]^-$, could have either a $\ldots\sigma^2, \sigma^{*1}$ structure with the extra electron largely confined to a Si–Si σ^* orbital, or it could distort to give:



Since the comparable radicals $[R_3P–PR_3]^+$ (R = alkyl) are known to have two equivalent, strongly coupled, phosphorus atoms,[22] the former structure is most probable. I have examined the e.s.r. spectra carefully for such an anion, but to no avail. It seems that the dissociation (10) is preferred, which, in view of the reverse reaction, (11), invariably detected for $[PR_3]^{+\cdot}$ radicals, is significant.

$$[F_3Si–SiF_3]^- \longrightarrow [{:}SiF_3]^- + SiF_3^{\cdot} \qquad (10)$$

$$[PR_3]^{+\cdot} + {:}PR_3 \longrightarrow [R_3P\dot{-}PR_3]^+ \qquad (11)$$

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[29] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 502.