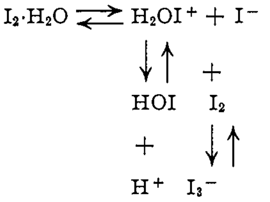
that although these reactions are more prominent at high *p*H values, they are important over the entire *p*H range studied.

To account for the observed phenomena the following mechanism is proposed. Let us consider that the first initial activity in the water layer is due to the partition of iodine and to reactions between iodine and water.

$$I_{2(CCl_4)} \rightleftarrows I_{2(H_2O)} \qquad (1)$$

$$I_2 + H_2O \rightleftarrows I_2\cdot H_2O \qquad (2)$$

At low concentrations reaction 2 would lie far to the right. To calculate the exact effect of this reaction on the distribution coefficient, the equilibrium constant would have to be known. However, the effect of this reaction would be seen at all *p*H values, which corresponds to the data obtained. Secondly, the slow rise in activity of the aqueous phase with time could be caused by the following dissociation of the water–iodine complex.

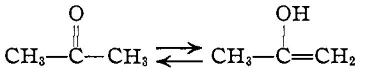


$$\begin{array}{lcl} I_2\cdot H_2O & \rightleftarrows & H_2OI^+ + I^- \\ & & \downarrow\uparrow \quad + \\ & & HOI \quad I_2 \\ & & + \quad \downarrow\uparrow \\ & & H^+ \quad I_3^- \end{array} \qquad (3)$$

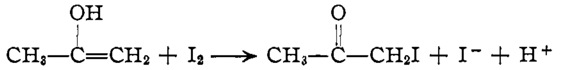
This equilibrium would be *p*H dependent due to the decomposition of H_2OI^+. Thus the equilibrium concentrations of HOI and I_3^- should decrease with a decrease in *p*H. This also is consistent with the data shown in Fig. 1.

The end products of the above reactions would be HOI and I_3^-. Since no iodate is found in the solutions, even after standing, apparently HOI is stable at these concentrations. The above mechanism would explain the gradual appearance of I_3^- and the increase in conductance with time in freshly prepared aqueous iodine solutions. A similar explanation has been given for the rise in conductance of iodine–pyridine solutions with time.[13,14]

This mechanism is also consistent with the results obtained by Benesi and Hildebrand[15] in a study of iodine–acetone solutions. They found that I_3^- was formed immediately when iodine was added to acetone. After observing the behavior and characteristics of these solutions they concluded that the following reactions were occurring



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftarrows CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \qquad (4)$$



$$CH_3-\overset{\overset{OH}{|}}{C}=CH_2 + I_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2I + I^- + H^+ \qquad (5)$$

$$I^- + I_2 \rightleftarrows I_3^- \qquad (6)$$

Equation 5 may be written stepwise to show complete analogy to eq. 3.

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(13) L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

(14) G. Kortüm and H. Wilski, *Z. physik. Chem.*, **202**, 35 (1953).

(15) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **72**, 2273 (1950).

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[CONTRIBUTION FROM THE PHYSICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Nuclear Magnetic Resonance Spectra of Some Perfluoroalkyl Derivatives of Sulfur Hexafluoride

BY NORBERT MULLER,[1] PAUL C. LAUTERBUR AND GEORGE F. SVATOS

RECEIVED SEPTEMBER 17, 1956

High-resolution F^{19} NMR spectra have been obtained for several perfluoroalkyl derivatives of sulfur hexafluoride of the types R_FSF_5 and $(R_F)_2SF_4$. Indirect spin-spin coupling leads to an unusually complex resonance multiplet for the F^{19} nuclei of the $-SF_5$ group. Calculations show that the observed fine structure is consistent with the assumption that these fluorines form a square pyramid. The resonance of the $-SF_4-$ group is a single line if the C–S–C angle is near 180°, and a characteristic pair of triplets if the C–S–C angle is near 90°.

Introduction

Compounds of the types R_FSF_5 and $(R_F)_2SF_4$ give F^{19} NMR signals in two, well-separated regions. One of these contains the resonances of the fluorine nuclei in the perfluoroalkyl (R_F) radical, which may be used to identify this radical. The other contains the resonances of fluorine bonded to the sulfur atom. A study of the multiplet patterns in this S–F region constitutes an interesting application of the theory of indirect spin–spin coupling.[2-4] We made a detailed analysis of the multiplet of the SF_5 group, using the method of reference 4; this required more precise calculations than the customary first-order approximation. The results are compatible with the supposition that the five fluorine atoms form a square pyramid. The pattern obtained for $-SF_4-$ groups was found to depend characteristically on whether the C–S–C angle is near 90° or near 180°.

Experimental

All materials used in these studies were prepared in these laboratories; methods of synthesis and purification are being published elsewhere.[5] The absence of NMR signals other than those which can be accounted for on the basis of the structures assumed for the materials indicates that no more than a few per cent. of fluorine-containing impurities can have been present in any of the samples.

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[1] Department of Chemistry, Purdue University, Lafayette, Ind.

[2] E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

[3] M. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc.* (*London*), **226A**, 490 (1954).

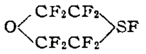
[4] H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23** 1152 (1955).

[5] F. W. Hoffmann, T. C. Simmons, *et al.*, to be published.

TABLE I

RESULTS OF F^{19} CHEMICAL SHIFT MEASUREMENTS

All entries are values of $\delta = (H_c - H_r)/H_r \times 10^6$, referred to CF_3COOH.

Group	$C_2F_5SF_5$	$C_3F_7SF_5$	$C_4F_9SF_5$	$(C_2F_5)_2SF_4$	$(C_3F_7)_2SF_4$	 $O\begin{matrix}CF_2CF_2\\CF_2CF_2\end{matrix}SF$
$-CF_3$	5.3	5.0	5.2	4.5	5.0	......
$C-CF_2-S$	15.5	18.8	18.0	21.2	16.5	22.2
$C-CF_2-C$	......	50.7	46.5	.....	50.0	......
			49.5			
$O-CF_2-C$	......	..	..	.....	.....	2.4
SF_5	-118.7^a -137.5	[b]	[b]	.....	.....	......
SF_4	......	..	..	-104.0	-106.1	-123.0^c -94.8

[a] These values are the δ-values for the base and apex fluorines of the SF_5 pyramid, derived from an analysis of the complex fine structure observed. [b] SF_5 resonance essentially the same as for $C_2F_5SF_5$. [c] These values are for the centers of the two triplet resonances arising from the non-equivalence of the fluorines in the SF_4 group of this molecule.

The NMR spectra were obtained with a commercial high-resolution NMR spectrometer[6] operating at a radiofrequency of 40 mc./sec., and using magnetic fields of the order of 10^4 gauss, provided by a 12" electromagnet system. Chemical shifts were measured by calibrating the sweep field using the method of Arnold and Packard.[7] The unit used is[8] $\delta = (H_c - H_r)/H_r \times 10^6$, where H_c and H_r are the resonance values of the field for the unknown and for the standard, respectively. CF_3COOH was used to produce the standard resonance, and the SF_4 signal from $(C_2F_5)_2SF_4$ was used as a secondary standard for resonances in the S–F region.

Results and Discussion

$CF_3CF_2SF_5$.—The chemical shifts of the nuclear resonances of $CF_3CF_2SF_5$ are given in Table I. The CF_3 and CF_2 resonances were identified by their positions and showed the expected intensity ratio 3:2. In this and all the other molecules studied, the signals due to CF_3 and CF_2 groups were somewhat broader than the resonance of CF_3COOH presumably because of indirect spin–spin interactions, but they could not be resolved into discrete components. As would be expected from previous work[9] on SF_6, the fluorines of the SF_5 group resonate at a considerably lower field than those of the R_F radical. In addition, their resonance shows an elaborate fine structure, indicating that the fluorine atoms are not in chemically equivalent positions.

The fluorine atoms in SF_6 are located at the points of a regular octahedron, and it is natural to assume that when an R_F radical is substituted for one of them the other five will form a square pyramid. The chemical shift would then probably be different for the four base fluorines as compared to the single apex fluorine atom leading to a double resonance with intensity ratio 4:1 for the two components.

At higher resolutions each component should show a further fine structure resulting from indirect spin–spin interactions between the base and apex atoms. By analogy with results[10] theoretically predicted and obtained for BrF_5 and IF_5, one would expect the stronger (base) signal to be split into a symmetrical doublet, and the apex signal into five equally spaced components with intensity ratios 1:4:6:4:1.

The positions of the lines actually observed are given in the first column of Table II. Roughly, the pattern consists of a strong doublet and a weak multiplet, but it does not conform in detail to the scheme discussed above. The components of the doublet are found to be broad and unequal in strength and the weak multiplet has nine components with irregular spacings and intensities.

TABLE II

FINE STRUCTURE OF THE RESONANCE FROM THE SF_5 GROUP OF $C_2F_5SF_5$ AT 40 MC./SEC.

Values are given in cycles/sec. relative to the SF_4 resonance of $(C_2F_5)_2SF_4$, and would be expected to vary with the applied field in a complex way. The observed intensities agreed qualitatively with the predicted ones.

	Shift		Calcd. relative intensity
	Obsd.	Calcd.	
	−1650	−1653	0.5
	−1546	−1545	0.6
	−1499	−1499	2.0
	−1420	−1422	0.7
Apex	−1369	−1370	2.7
Atoms	−1341	−1341	2.0
	−1277	−1279	1.1
	−1212	−1212	4.3
	−1089	−1089	2.2
		− 668	5.1
		− 659	7.3
		− 654	7.2
	− 645 (broad)	− 649	7.4
		− 646	6.9
Base		− 640	4.5
Atoms		− 532	3.5
		− 524	5.1
	− 505 (broad)	− 519	4.9
		− 510	4.8
		− 501	4.7
		− 479	2.8

The cause of this discrepancy becomes apparent if a detailed analysis of the spin–spin interaction is undertaken,[11] using the procedure which is given in

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[6] The spectrometer and magnet system were purchased from Varian Associates, Palto Alto, California, from whom data on the characteristics of this equipment may be obtained.

[7] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[8] There is as yet no unanimity in the literature as to the sign to be used in defining δ. See J. N. Shoolery and H. E. Weaver, *Ann. Rev. Phys. Chem.*, **6**, 439 (1955).

[9] H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

[10] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *ibid.*, **21**, 279 (1953).

[11] We are indebted to a referee for pointing out that our observed pattern is of the form shown in Fig. 7 of ref. 3. This reference was not available to us at the time this work was done. The four lines at the far right in the figure just referred to were ignored in our treatment since their intensity should be very small, and indeed no such lines were observed.

reference 4. The energy levels between which transitions occur are obtained as eigenvalues of a secular determinant containing both diagonal and off-diagonal terms. If $(\delta_A - \delta_B)$, the difference in chemical shift between the interacting nuclei, is much larger than the interaction constant J_{AB}, the off-diagonal terms become negligible; this leads to the simple pattern found for BrF_5 and IF_5, with equally spaced components whose separation is numerically equal to J_{AB}.

In the present problem $|\delta_A - \delta_B| \cong 5J_{AB}$ and the observed pattern can only be accounted for if the off-diagonal terms are included in the calculation. Explicit formulas for the energy levels in terms of δ_A, δ_B and J_{AB} can be derived if a value is assumed in advance for the ratio $|\delta_A - \delta_B| : J_{AB}$. We found such formulas, using the value 5.0 for this ratio. The best fit of the observed spectrum is then obtained with the values $\delta_A = -137.5$ (apex atoms), $\delta_B = -118.7$ (base atoms) and $J_{AB} =$ 145 cycles/second, or 3.63 units of δ under the conditions we used. The actual ratio $|\delta_A - \delta_B|: J_{AB}$ is then 5.18, quite near the value taken. The calculated shifts are given in the second column of Table II and the corresponding intensities in the third column. Although intensities are difficult to measure precisely, the agreement both between predicted and observed shifts and intensities is excellent.

The spectrum does not show any additional splitting due to interaction of fluorines in the CF_2 group with those of the SF_5 group. The corresponding interaction parameter must be very nearly zero.

$C_3F_7SF_5$ and $C_4F_9SF_5$.—Chemical shifts for the main resonance peaks of these compounds are included in Table I. The number of peaks depends as expected on the length of the R_F chain, while the spectrum of the SF_5 group is essentially the same as for the perfluoroethyl derivative.

$(C_2F_5)_2SF_4$ and $(C_3F_7)_2SF_4$.—The chemical shifts of the peaks of these materials are given in Table I. The signals from the R_F radicals occur at nearly the same fields as these in the corresponding R_FSF_5 compounds. The fluorines of the SF_4 group give rise to a single resonance (a convenient secondary reference resonance for the SF_x region). This indicates that the four fluorines are equivalent, and is consistent with the supposition that the C–S–C angle is 180° with the fluorines of the SF_4 group in a plane. Again there is no indication of splitting between fluorines in the R_F radical and fluorines bonded to sulfur.

$\overline{CF_2CF_2OCF_2CF_2S}F_4$.—The peaks found for this cyclic compound are shown in Table I. The two $-CF_2-$ resonances were identified by comparing the shifts with those of the open-chain derivatives. The spectrum of the SF_4 group now consists of two main signals, each of which is split into a triplet by the indirect spin–spin interaction.

This pattern arises because of the fact that the C–S–C angle in this material must be of the order of 90°. The fluorines of the SF_4 group are then no longer equivalent, two of them being approximately in the C–S–C plane, while the other two are above and below it. Each pair will give rise to a signal split into a triplet by the interaction from the other pair. The observed pattern conforms fairly well to the simple form expected when $|\delta_A - \delta_B| >> J_{AB}$; we found $\delta_A = -123.0$, $\delta_B = -94.8$ $J_{AB} = 93$ cycles/sec. (or 2.3 δ-units) so that $|\delta_A\text{-}\delta_B| = 12.2J_{AB}$. The data do not allow one to decide which δ-value corresponds to which pair of fluorine atoms.

The absence of a pattern like the one just described in the spectra of the open-chain $(R_F)_2SF_4$ compounds seems a clear indication that only the 180° form was present in the samples studied.

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

A Precise Correlation of Nuclear Magnetic Shielding in *m*- and *p*-Substituted Fluorobenzenes by Inductive and Resonance Parameters from Reactivity

BY ROBERT W. TAFT, JR.

RECEIVED AUGUST 29, 1956

Gutowsky's F^{19} nuclear magnetic shielding parameters, δ^F, for *m*- and *p*-substituted fluorobenzenes are precisely correlated by the equations $\delta^F m = (0.583 \pm 0.026)(\sigma_I) - 0.02$ and $\delta^F p = (0.583)(\sigma_I) + (1.880 \pm 0.081)(\sigma_R) - 0.08$. σ_I and σ_R are inductive and resonance parameters, respectively, obtained recently by Taft from a quantitative separation of Hammett σ-values to inductive and resonance contributions. This correlation provides an experimental proof that (1) reaction rates and equilibrium which follow precisely the Hammett equation, $\log (k/k_0) = \sigma\rho$, are determined quantitatively by the effects of the substituent on the electron distribution; and (2) the values of σ_I and σ_R are quantitative and independent measures of the electron-withdrawing effects of substituents through inductive and resonance interactions, respectively.

It has been generally accepted that the σ-values of Hammett (obtained from the ionization constants of *m*- and *p*-substituted benzoic acids) are quantitative free energy measures of the effect of the substituent on the electron distribution (polar effect) in many derivatives of benzene.[1] More recently, it has been proposed that the shielding effects, δ^F, measured by Gutowsky, *et al.*, from the nuclear magnetic resonance lines of *m*- and *p*-substituted fluorobenzenes provide quantitative measures of these effects.[2] Gutowsky, *et al.*, have found, however, that although a plot of δ^F *vs.* σ (*cf.* Fig 1) shows an unmistakable trend toward

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[1] (a) L. P. Hammett, *Chem. Revs.*, **17**, 125 (1953); (b) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York N. Y., 1940, p. 184; (c) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[2] (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); (b) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).