

and, letting $X = [A_n]$

$$K = \frac{X}{(A_0 - nX)^n} \quad (\text{II-1})$$

and

$$\delta_{\text{obsd}} = \frac{nX\Delta_{A_n}}{A_0} \quad (\text{II-2})$$

There are several studies in the literature, primarily of strongly associated species such as alcohols, in which the assumptions and approximations needed to determine n are discussed.^{22, 37, 38} A general and precise graphical method for determining the value of n for such equilibria is discussed below.

We shall use an indirect method to generate a log-log plot of reduced variables. Substituting $\rho = \delta_{\text{obsd}}/\Delta_{A_n}$ into eq II-2, solving for X , and substituting this expression into eq II-1 and rearranging, we have

$$K_{A_n} A_0^{n-1} = \frac{\rho}{n(1-\rho)^n} \quad (\text{II-3})$$

(37) L. A. LaPlanche, H. B. Thompson, and M. T. Rogers, *J. Phys. Chem.*, **69**, 1482 (1965).

(38) P. O. P. Ts'O and S. I. Chan, *J. Am. Chem. Soc.*, **86**, 4176 (1964).

then

$$\alpha = \left[\frac{\rho}{n(1-\rho)^n} \right]^{1/(n-1)}$$

where

$$\alpha = \varphi A_0, \text{ and } \varphi = K_{A_n}^{(1/n-1)}$$

Rather than solving for ρ in terms of α , it is only necessary to select convenient values of ρ and calculate the unique values of α associated with them (for each n). Figure 9 presents log-log plots of ρ vs. α for $n = 2, 3$, and 4. To determine whether a single monomer- n -mer equilibrium describes the observed chemical shifts, one compares a plot of $\log \delta$ vs. $\log A_0$ to the plots for various n 's. Δ_{A_n} can then be found as before. K_{A_n} is calculated from

$$K_{A_n} = \varphi^{n-1} \quad (\text{II-4})$$

From eq II-3 we see that the limiting slope of a plot of $\log \rho$ vs. $\log \alpha$ as $\rho \rightarrow 0$ is $n - 1$. Thus log-log plots yield n , Δ , and K for the monomer- n -mer equilibria.

Dynamic Enhancement of Fluorine Nuclear Magnetic Resonance Signals. Some Effects of Chemical Environment

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Abstract: Dynamic polarization of fluorine nuclei in free-radical solutions (diphenylpicrylhydrazyl and galvinoxyl) has been studied for a selection of fluorocarbons of different chemical nature. The observed nmr enhancements and the amount of scalar coupling, due to electron density at the F nucleus, are shown to vary considerably upon change of radical or fluorocarbon. Aromatic fluorocarbons always show higher scalar rates than do saturated compounds. The halo-substituted fluorobenzenes show regular trends indicative in part of complicated π -system interactions. Exchange polarization, after the manner of coupling on free radicals, and complex formation appear to be the dominant mechanisms producing the observed effects.

In contrast to hydrogen,¹ the dynamic polarization of fluorine nuclei is extremely sensitive to the detailed chemical environment of the resonating nucleus. Observed ¹⁹F nmr enhancements are governed by the type of free radical and fluorocarbon present.² Moreover, the presence of an additional nonfluorine-containing compound in the system can strongly influence the signal strength.³ Because the interactions between these species become exceedingly complex when all three are varied independently, we have limited ourselves here primarily to the presentation of detailed experimental results for systems designed to isolate variations in polarization arising from different fluorocarbons interacting with a given radical, diphenylpicrylhydrazyl (DPPH). The fluorocarbons used not

only demonstrate the range of nmr enhancements to be expected for F in different chemical environments, but also lead to generalizations which relate observed enhancements to the aromatic character of the fluorocarbon, to the position of the ¹⁹F nucleus in aromatic isomers, and to the number of F atoms in a given compound. In addition, the effects of NO₂, I, Br, and Cl as substituents are investigated.

Theoretical interpretation of the results is not straightforward. We present data for a selection of fluorobenzenes in DPPH and galvinoxyl (GALV) which demonstrate that relative enhancements within a series of fluorocarbons can change drastically upon change of radical. This, when coupled with our previous results² for hexafluorobenzene with various radicals, shows that any comprehensive theory must not be restricted to interpretations arising solely from the ground-state properties of the radical or the fluorocarbon: interactions between the two must be con-

(1) W. Muller-Warmuth, *Z. Naturforsch.*, **21a**, 153 (1965).

(2) E. H. Poindexter, J. R. Stewart, and P. J. Caplan, *J. Chem. Phys.*, in press.

(3) E. H. Poindexter and J. R. Stewart, unpublished results.

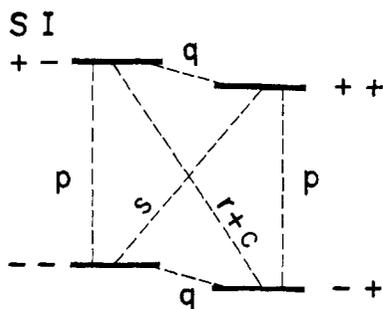


Figure 1. Spin states and relaxation transitions for weak-field electron-nucleus interaction.

sidered specifically. Such a treatment requires detailed knowledge of the ground- and excited-state wave functions of the molecules. We are presently engaged in molecular orbital calculations, which, when supplemented by spectral analysis (nmr, epr, ultraviolet) of the various species, should help determine the relative importance of radical and fluorocarbon in predicting enhancements and lead to a semiquantitative explanation of our results.

Theory

Although the ratio of free electrons to nuclei in a typical liquid sample is small, it is reasonable to consider the interaction of a single electron with a single nucleus. In liquids, unlike the solid-state case,⁴ electronic relaxation deficiency cannot "bottleneck" the nuclear polarization, and rapid tumbling motions permit the individual nuclei to be treated as if they were unaware of their competition for the electron. The spin states for an electron interacting with a magnetic nucleus in a weak magnetic field are shown in Figure 1. Molecular motions modulate the spin-spin coupling inducing relaxation transitions which are of two types: dipolar and scalar (contact). The dipolar transition probabilities, p , q , r , and s , can be derived from classical dipole interactions while the contact or scalar rate, c , due to electron spin density at the nucleus, is usually treated quantum mechanically. The normal strength of the nmr signal is proportional to the population difference

$$(n_{-+} + n_{+-}) - (n_{++} + n_{--})$$

and is affected by the relative magnitudes of the various transitions. Dynamic polarization is produced when electron transitions parallel to p are stimulated with a strong radiofrequency source. The resultant nmr enhancement is given by

$$G = \frac{A}{A_0} - 1 = \frac{\gamma_e (r - s + c) N_e S_e(P)}{\gamma_n (2q + r + s + c) N_e + R_B} \quad (1)$$

where G , the signal enhancement, is the quantity used in discussing the magnitude of the polarization; A , the enhanced nmr amplitude, is the quantity actually observed relative to the unenhanced nmr signal A_0 ; γ_e and γ_n are the gyromagnetic ratios for the electron and nucleus, respectively; N_e is proportional to the number of unpaired electrons per cc; R_B is the bulk relaxation rate of the nuclei with no radical present; and $S_e(P)$ is the electron saturation function. For H, $\gamma_e/\gamma_n = 658$, for F, 700. It is desirable to remove the

(4) C. D. Jeffries, "Dynamic Nuclear Orientation," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

dependence of G on electron concentration and radiofrequency power. For this reason, values of G are extrapolated to infinite power and infinite radical concentration. The electron saturation function approaches unity at infinite power and we obtain the extrapolated enhancement

$$G_{\infty, \infty} \equiv U_{\infty} = \frac{\gamma_e (r - s + c)}{\gamma_n (2q + r + s + c)} \quad (2)$$

from which it is seen that U_{∞} may be positive, negative, or zero depending upon the relative sizes of q , r , s , and c . At zero field, the values of q , r , and s are 3, 2, and 12, respectively. Their values at 74 gauss (3.0, 1.6, and 9.6) were determined from dipolar diffusion curves⁵ based on a correlation time of 3×10^{-11} sec. We have previously shown² that reasonable differences in correlation time will have little effect on c . Given q , r , and s , measurement of U_{∞} leads to a unique scalar rate *via* eq 2. If $c = 0$, the theoretical limit of U_{∞} becomes -310 for H and -330 for F.

Experimental Section

All dynamic polarization measurements were made at room temperature ($24 \pm 1^\circ$) in a magnetic field of 74 gauss for which $\gamma_H = 319.7$ kc, $\gamma_F = 300.8$ kc, and $\gamma_e = 210.7$ Mc. The epr line of DPPH was stimulated by a 100-w transmitter capable of rapid on-off switching to permit measurements of nuclear relaxation times by signal growth and decay. A marginal oscillator was used for nmr detection. A more extensive treatment of the apparatus is given elsewhere.²

DPPH was chosen to test the effects of chemical environment because of its availability, stability in solution, and well-known epr parameters. Because of its low solubility in many of the fluorocarbons used, a radical concentration of 0.01 M was used for all samples. At this concentration, the DPPH epr line was broad and could not be saturated with our transmitter. However, since proton enhancements approach -310 (the theoretical value in benzene at 74 gauss) for DPPH concentrations ≥ 0.04 M , ultimate F enhancements were deduced from the measured ratios of F to H enhancements, assuming -310 for H. This gave values within the scatter of the data, since H has been shown^{1,2} to exhibit little scalar coupling in any solution.

Although additional solvents affect the ultimate enhancement, it was not possible to remove them entirely because of the low solubility of DPPH. Whenever possible, we tried to use the same solvent for a given class of compounds, thus normalizing the effect if not isolating it. Fluorocarbons were chosen on the basis of their stability in DPPH as well as for the trends they were designed to isolate. Unfortunately, a number of interesting compounds were either gaseous (halo-substituted ethanes and propanes) or reacted with DPPH (fluorophenols, fluoroanilines) and could not be studied, limiting the detail of our results in some cases.

Results

Aliphatics. Fluorine scalar rates for saturated fluorocarbons are shown in Table I, from which it is seen that F atoms not adjacent to double bonds give rise to relatively modest scalar rates in the range 1.8 to 3.0. Neither the number of F atoms per compound nor the chemical nature of the fluorocarbon has a great effect on the enhancement. The effects of substituents are not clear, owing in part to the paucity of data. However, the small differences in c_F might be related to the inductive strength of the substituent group (*cf.* 1,2-dichloro-1,2-difluoroethane and 1,2-difluoro-1,1,2,2-tetrachloroethane).

Fluorobenzenes. In Table II and Figure 2, scalar rates for a variety of fluorobenzenes are shown. With

(5) K. D. Kramer and W. Muller-Warmuth, *Z. Naturforsch.*, **19a**, 375 (1964).

Table I. ^{19}F Nmr Enhancements for Aliphatic Fluorocarbons in DPPH^a

Fluorocarbon	Additional solvent	U_∞	c_F
1,1,1-Trifluoro-2,2,2-trichloroethane	50% acetone	-235	1.8 (0.2)
1,2-Dichloro-1,2-difluoroethane	None	-170	3.1 (0.2)
1,2-Difluoro-1,1,2,2-tetrachloroethane	50% acetone	-180	2.8 (0.2)
1,1,2,2-Tetrafluoro-1,2-dibromoethane	50% acetone	-230	1.8 (0.2)
α,α,α -Trifluorotoluene	None	-185	2.7 (0.2)
Perfluoro- <i>n</i> -hexane	5% acetone-- 90% CCl_4	-205	2.3 (0.2)
1-Fluoro- <i>n</i> -octane	None	-190	2.6 (0.2)
Perfluorocyclohexane	5% acetone-- 90% CCl_4	-240	1.6 (0.1)
Perfluorodecalin	5% acetone-- 90% CCl_4	-200	2.4 (0.2)
1,2,4-Trifluorobromobutene	None	-170	3.0 (0.2)

^a In this and in subsequent tables, standard errors for c_F are given in parentheses. All scalar rates are per F atom.

DPPH as the pumping source, the average scalar rate per F atom increases with the number of fluorines present, while for GALV, no such trend is noted. This affords striking proof that the fluorocarbon alone cannot determine the degree of dynamic polarization.

Table II. ^{19}F Nmr Enhancements for Fluorobenzenes in DPPH and GALV

Fluorocarbon	Additional solvent	U_∞		c_F	
		DPPH	GALV	DPPH	GALV
Fluorobenzene	None	-170	-195	3.1 (0.2)	2.5 (0.2)
<i>o</i> -Difluorobenzene	None	-170	-205	3.1 (0.2)	2.3 (0.2)
<i>m</i> -Difluorobenzene	None	-160	-195	3.3 (0.1)	2.5 (0.1)
<i>p</i> -Difluorobenzene	None	-180	-215	2.9 (0.1)	2.1 (0.1)
1,2,4-Trifluorobenzene	None	-155	-200	3.5 (0.2)	2.4 (0.2)
1,2,3,4-Tetrafluorobenzene	None	-130	-205	3.5 (0.2)	2.4 (0.2)
1,2,3,5-Tetrafluorobenzene	50% C_6H_6	-120		4.3 (0.1)	
1,2,4,5-Tetrafluorobenzene	None	-110	-200	4.5 (0.1)	2.4 (0.1)
Pentafluorobenzene	None	-95	-215	5.0 (0.1)	2.1 (0.1)
	50% C_6H_6	-75		5.6 (0.1)	
Hexafluorobenzene	None	-2	-200	8.0 (0.1)	2.4 (0.2)
	50% C_6H_6	-13	-200	7.5 (0.1)	2.4 (0.3)
	50% acetone	-40	-150	6.6 (0.3)	3.5 (0.3)

Disubstituted Benzenes. Directed Substitution.

Table III and Figure 3 include scalar rates for *ortho*-, *meta*-, and *para*-substituted monofluorobenzenes. In all cases, *meta* substitution produces the highest scalar rate. For the *meta* and *para* cases, the order of increasing scalar rate is $\text{F} < (\text{Cl} \sim \text{Br}) < \text{I} < \text{NO}_2$, while for the *ortho* case, the corresponding order is nearly inverted: $\text{I} < (\text{Cl} \sim \text{Br}) < \text{F} < \text{NO}_2$. Thus, a decided *ortho* effect exists.

Substituted Penta- and Tetrafluorobenzenes. Table IV shows c_F for halogen-substituted tetra- and pentafluorobenzenes; the order of increasing scalar rate per F here is $\text{H} < \text{I} < \text{Br} < \text{Cl} < \text{F}$, in general agree-

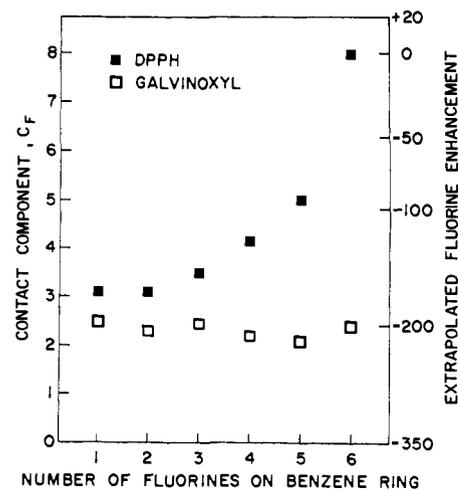
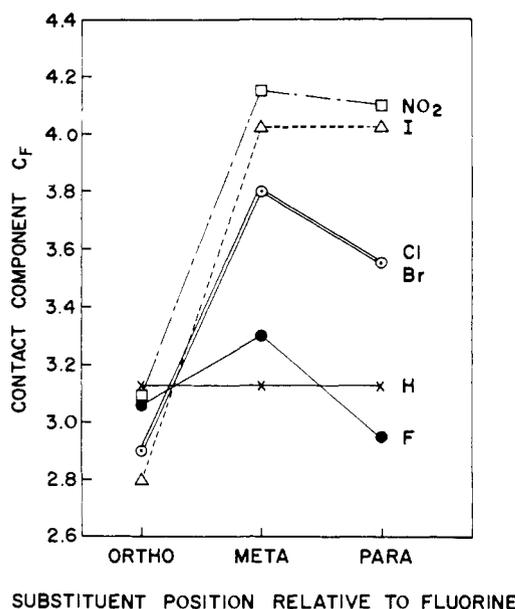
Figure 2. ^{19}F nmr enhancements for fluorobenzenes in DPPH and GALV.

Figure 3. Fluorine contact coupling in substituted fluorobenzenes with DPPH.

ment with the trend observed for the *o*-halofluorobenzenes. We note that the observed rates for the tetrafluoro species are lower than those for the penta-

Table III. ^{19}F Nmr Enhancements for Disubstituted Benzenes in DPPH^a

Fluorocarbon	U_∞	c_F
<i>o</i> - $\text{C}_6\text{H}_4\text{F}_2$	-170	3.1 (0.1)
<i>m</i> - $\text{C}_6\text{H}_4\text{F}_2$	-160	3.3 (0.1)
<i>p</i> - $\text{C}_6\text{H}_4\text{F}_2$	-180	2.9 (0.1)
<i>o</i> - $\text{C}_6\text{H}_4\text{FCl}$	-180	2.9 (0.1)
<i>m</i> - $\text{C}_6\text{H}_4\text{FCl}$	-145	3.8 (0.1)
<i>p</i> - $\text{C}_6\text{H}_4\text{FCl}$	-150	3.6 (0.1)
<i>o</i> - $\text{C}_6\text{H}_4\text{FBr}$	-180	2.9 (0.1)
<i>m</i> - $\text{C}_6\text{H}_4\text{FBr}$	-140	3.8 (0.1)
<i>p</i> - $\text{C}_6\text{H}_4\text{FBr}$	-150	3.6 (0.1)
<i>o</i> - $\text{C}_6\text{H}_4\text{FI}$	-185	2.8 (0.1)
<i>m</i> - $\text{C}_6\text{H}_4\text{FI}$	-130	4.0 (0.1)
<i>p</i> - $\text{C}_6\text{H}_4\text{FI}$	-130	4.0 (0.1)
<i>o</i> - $\text{C}_6\text{H}_4\text{F}(\text{NO}_2)$	-170	3.1 (0.1)
<i>m</i> - $\text{C}_6\text{H}_4\text{F}(\text{NO}_2)$	-125	4.2 (0.1)
<i>p</i> - $\text{C}_6\text{H}_4\text{F}(\text{NO}_2)$	-130	4.1 (0.1)

^a No additional solvent added in any case.

Table IV. ^{19}F Nmr Enhancements for Halo-Substituted Tetra- and Pentafluorobenzenes in DPPH^a

Fluorocarbon	U_{∞}	c_F
Hexafluorobenzene	-15	7.5 (0.1)
1,2-Dibromotetrafluorobenzene	-40	6.6 (0.1)
1,2-Diiodotetrafluorobenzene	-55	6.2 (0.2)
Chloropentafluorobenzene	-25	7.1 (0.1)
Bromopentafluorobenzene	-35	6.8 (0.1)
Iodopentafluorobenzene	-50	6.4 (0.1)

^a Additional solvent, 50% C_6H_6 , added in each case.

fluoro compounds, the same order as the parent compounds.

Aliphatic vs. Aromatic Character. Fluorine atoms which share in a delocalized π system quite generally show higher scalar rates than those not adjacent to double bonds. This effect appears general, extending beyond the results presented here, *i.e.*, to any class of fluorocarbons for any given radical. The nature of the fluorocarbon π orbitals, then, may provide an important clue for the explanation of our results.

Discussion

A number of models have been proposed to account for dynamic polarization results, the most common of which are the diffusion and sticking models.^{6,7} Both theories relate differences in nmr enhancements to diffusion constants and the distance of closest approach of radical and solvent. The time dependence of the interaction arises from the translational motions of the molecules. The sticking model has the added advantage of considering complex formation in solution leading to additional dipolar modulation by rotational tumbling. Neither theory, however, explicitly considers the nature of the interaction from a chemical standpoint. This, we feel, is a major reason for the discrepancies between theory and experiment noted⁸ in some cases. In what follows, we assume that the dipolar part of the enhancement is adequately described by the above models and concentrate on mechanisms that lead to different scalar components.

Contact coupling between a radical electron and a magnetic nucleus attached to another molecule may be effected by two mechanisms. Spin information can be transmitted to the nucleus indirectly by exchange polarization of the fluorocarbon molecular orbitals as they overlap the radical electron during collision. The second possibility involves charge transfer from radical to solvent by the formation of either a transient or long-lived complex. The major difference between these possibilities is the time scale of the interaction. Collisional processes would be expected to occur with a frequency well described by the laws of diffusion, while the time of interaction for complex formation should vary considerably as the chemical composition of the system is changed.

An explanation of exchange polarization has been given by McConnell,⁹ who showed that appreciable spin density can appear at a proton of an aromatic free

(6) G. J. Kruger, W. Muller-Warmuth, and R. Steenwinkel, *Z. Naturforsch.*, **21a**, 1224 (1966).

(7) R. A. Dwek, J. G. Kenworthy, J. A. Ladd, and R. E. Richards, *Mol. Phys.*, **11**, 287 (1966).

(8) J. G. Kenworthy, J. A. Ladd, and R. E. Richards, *ibid.*, **11**, 469 (1966).

(9) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

radical when the odd electron is in a π molecular orbital (MO). In his treatment, the odd electron is stabilized by the tendency of the electrons in a C-H σ bond to become unpaired. This π - σ polarization leads to an expression relating the effective spin density at the proton to that in the odd-electron π MO. A similar expression has been used¹⁰ to interpret the F hyperfine coupling constant in the epr spectrum of tetrafluoro-*p*-benzosemiquinone, but further refinement¹¹ to include spin density in the $2p\pi$ F orbital was found to be necessary for a complete treatment. The fluorocarbon orbitals and the free-radical electron orbital may be considered in a similar fashion as a simple system during the molecular encounter, but, because the odd electron and the magnetic nucleus are no longer on the same compound, polarization depends upon the relative orientation and time of contact of the colliding species. Since F participates in the π system of aromatic fluorocarbons, direct polarization can take place between the π orbitals and the hybrid orbitals about the F nucleus. A similar effect can be obtained by polarization of the hybrid orbitals themselves; this, of course, cannot take place for H. Furthermore, the greater electronegativity and spatial extent of the F orbitals can lead to more effective overlap with the radical orbital and thus to a higher scalar rate for F as compared with H.

The exchange polarization model offers an explanation for the differences in enhancement between aromatic and aliphatic fluorocarbons. By this mechanism, the scalar rate for saturated compounds could only arise by the unfavorable⁹ transmission of spin information through the σ -bonding system for a collision removed from the F atom, or by direct contact of the radical with the F electrons. Thus, the number of successful collisions for a solution deficient in radicals would be small, leading to a low scalar rate. Differences in enhancement for a given aliphatic would then be due primarily to the availability of the free electron. In unsaturated compounds, the mobile π electrons can also be polarized by the radical and the scalar effect can be transmitted over a distance, making many more collisions fruitful.

Complex formation, the second mechanism, occurs when the electrons of the two molecules become delocalized or redistributed upon association. Quadrupole resonance studies¹² of stable complexes indicate that little charge is transferred for some complexes, but a transfer or intramolecular redistribution of 0.01 e would be more than enough to produce the observed scalar rates provided that the life of the complex is of the order of 10^{-9} sec. Complexes have been found^{13,14} to be responsible for solvent effects on the hyperfine splittings in epr spectra; the solvent is assumed to alter the electronegativity of a radical functional group, thereby redistributing the odd electron and changing the hyperfine splitting. Changes in spin density upon complexation¹³ are of the order of 0.01 e. Charge-transfer complexes have been interpreted¹⁵ on the basis of interactions between π

(10) D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *ibid.*, **32**, 196 (1960).

(11) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(12) H. O. Hooper, *J. Chem. Phys.*, **41**, 599 (1964).

(13) E. W. Stone and A. H. Maki, *J. Am. Chem. Soc.*, **87**, 454 (1965).

(14) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

orbitals of the two molecules; the effective strength of the interaction is inversely proportional to the energy difference of the orbitals concerned. If charge is transferred, the direction is from radical to solvent if the donor energy level is higher than the acceptor level or from solvent to radical if the reverse is true, but direction is not the overriding consideration here since spin density of the same sign would appear on the solvent in either case for a radical of given spin. The degree of interaction and the resulting charge distribution cannot be predicted, of course, without specific knowledge of the required orbitals.

The charge transfer or complex model also offers an explanation for the observed differences between aliphatic and aromatic fluorocarbons. Since σ orbitals do not in general lead to complex formation, aliphatics should have lower scalar rates if this mechanism is dominant. Indeed, the fact that high scalar rates are observed² for relatively planar radical anions and cations, for which stabilization by charge delocalization would be favored, is strongly suggestive of complex formation or at least of preferential orientation upon collision.

Charge transfer is also successful in explaining the fundamental difference between F and H enhancements. A large scalar rate for H on C₆H₆ with DPPH might be expected if a complex is formed, but this is not found.² The creation of a virtual radical by transfer should lead to hyperfine splittings on the solvent which are analogous to those of stable, permanent free radicals. Observed hyperfine couplings for F average about a factor of 2 greater than those for H in a few comparable situations;¹⁶ this should produce contact relaxation rates for F nuclei which are four times those for H. Thus, fairly substantial scalar rates might be expected for H now and again, whereas the observed rates are always at least an order of magnitude below those for F in analogous situations. This difference can be attributed to preferential or additional complexation at F through the $2p\pi$ fluorocarbon orbitals.

The regular increase in c_F for the fluorobenzene series with DPPH could be due to different degrees of complexation or exchange polarization. If it is assumed that exchange polarization is more likely the higher the energy of the highest filled fluorocarbon MO while charge transfer increases as the energy of the lowest unoccupied MO decreases, then, on the basis of selected ionization potentials,¹⁷ the F effect is inconsistent. However, the effect may be more complicated, involving many of the molecular orbitals. The absence of such an increase for GALV could arise from the four *t*-butyl groups on the molecule which can shield the electron from the fluorocarbon, preventing complex formation. Similarly, the same groups could

reduce the effective amount of polarization during collision. Over-all, the results for GALV are reminiscent of those for aliphatic fluorocarbons with each F nucleus acting relatively independently of the others. Thus, there is evidence for weak transmission of spin information through the fluorocarbon π system for GALV and corresponding strong transmission for DPPH. The fact that for both radicals the order of c_F for *o*-, *m*-, and *p*-difluorobenzene, and for the tetrafluorobenzenes, is the same indicates that isomeric differences are independent of the choice of radical; *i.e.*, they are primarily a property of the fluorocarbon itself.

In discussing the effects of directed substitution, the concept of free valence,¹⁸ which describes the number of π electrons able to interact with an approaching spin, might be more useful than charge density arguments since the *meta*-directing NO₂ group shows the same general trend as do the *ortho-para*-directing halogens. The large reduction in scalar rate for the *o*-dihalobenzenes might result mostly from steric hindrance in analogy with the reactivity¹⁹ and spectral interpretation^{20,21} of such species. The heavier halogens should be more polarizable than the lighter ones, in agreement with the data for the unhindered *meta* and *para* isomers. The halo-substituted tetra- and pentafluorobenzene results can also be interpreted on the basis of steric shielding. Iodine atoms are expected to be most out of the plane of the benzene ring, making them least able to interact with F *via* the π system. The effect would diminish as the size of the halogen decreases, leading to the highest scalar rate for the F-substituted compounds. It would be interesting to see if this trend persists for GALV where π interactions are expected to be minimal.

To summarize, we feel that both complexation and exchange polarization are important in determining the nmr enhancement for a given radical-fluorocarbon system. In order to separate these effects and to determine the importance of each for a given system, we propose a series of studies which include: (1) measurement of enhancements for a series of monofluoroalkanes with various radicals (since complex formation is not expected for these compounds, the observed scalar rates should be proportional to the effective number of collisions after the relative rates of diffusion are taken into account; these results might then lead to a polarization base line for each radical to which the effects of complexation could be added); (2) measurement of c_F and contact times for systems at different temperatures (the enhancement should change with temperature in a manner different from that predicted on the basis of diffusion and viscosity alone if complexation occurs); (3) an intensive investigation into the spectral properties and molecular orbitals for simple radicals and fluorocarbons with the hope that empirical or semiquantitative generalizations relating molecular properties to enhancement emerge.

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