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Authors

Ng, Soon

Tang, Jane

Sederholm, C.H.

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Ernest O. Lawrence
Radiation Laboratory

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July 1964

THE EFFECT OF SOLVENTS ON F^{19}
SPIN-SPIN COUPLING CONSTANTS

Soon Ng,^{*} Jane Tang,[†] and C. H. Sederholm

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Chemistry, College of Chemistry
University of California, Berkeley, California

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ABSTRACT

The effect of solvents on the coupling constants of the compounds, $CF_2=CFBr$, CF_3CFCl_2 , and $CF_2BrCFBrCl$, has been studied. The coupling constants are found to vary with the solvents. This implies that intermolecular interactions affect coupling constants to a degree that is not negligible. The variations in the coupling constants are to some extent correlated with the size, electronic character, and dipolar nature of the solvent molecules. The temperature dependence of fluorine coupling constants that has been reported previously may be due to this temperature dependent molecular interaction as well as the population of excited vibrational states.

[†]Present Address: Department of Chemistry, Cornell University,
Ithaca, New York.

^{*}Present Address: Department of Chemistry, University of Malaya,
Kuala Lumpur, Malaya.

INTRODUCTION

The factors influencing nuclear magnetic resonance (NMR) coupling constants and chemical shifts, while of great significance, are not well understood. In compounds, substituted ethanes in particular, in which rotational averaging occurs, it has been assumed by several investigators^{1, 2} that each rotamer has associated with it a simple set of chemical shifts and coupling constants, and that the high temperature, time-weighted spectrum can be calculated from these sets of parameters for the several exchanging isomers. In fact, Gutowsky, Belford, and McMahon¹ using infrared determined energy differences between rotamers, have tried to determine the chemical shifts, and coupling constants in each rotamer of some substituted ethanes by least squares fitting of the high temperature spectra. This procedure assumes that the observed temperature dependence of the high temperature spectrum arises only from changes in the equilibrium populations of the isomers and that coupling constants and chemical shifts have no intrinsic temperature dependence. However, recently Brey and Ramey³ have observed the temperature dependence of the fluorine coupling constants of some fluoro-organic compounds which exist as one isomer. They attributed this temperature dependence of the coupling constants to population of higher torsional and other vibrational states, giving larger weight to angles and atomic positions not corresponding to the equilibrium configuration. Brey and Ramey⁴ subsequently reported that molecular interactions have negligible effect on the coupling constants by studying the solvent effect of two solvent both of which were similar to the solute.

Newmark and Sederholm² have studied the time-weighted-average approximation in the NMR spectrum of $\text{CF}_2\text{BrCFBrCl}$ and found that there is a discrepancy of the order of 10% between the calculated, high temperature and the observed, averaged coupling constants. They attributed this discrepancy to either population of excited torsional states or temperature dependent molecular interactions.

Hitherto, it has been postulated that different solvents affected coupling constants through changes in (a) the relative energies of two or more rapidly equilibrating isomers whose time-averaged coupling constants are being observed, or (b) the bond order of the bond connecting the coupled nuclei.^{5, 6} The first effect cannot be operative in molecules like CF_3CFCl_2 in which the CF_3 unit has three-fold symmetry. The second effect has been called upon to explain the magnetic resonance measurements on solutions of formamide (HCONH_2) in acetone and in water, in which there was unusual medium dependence of the proton coupling constants.⁶ This dependence of the coupling constant on solvents probably arises as a result of changes in the molecular geometry and/or the molecular charge distribution, induced by intermolecular interactions, which in formamide must be primarily hydrogen-bonding. In molecules in which hydrogen-bonding is not possible, the possibility still exists that weak molecular interactions may give rise to temperature dependent NMR spectral parameters. This same mechanism should result in NMR parameters which vary in different solvents. The purpose of this work was to determine the magnitude of such solvent effects in a wider variety of solvents than was used by Brey and Ramey.⁴

EXPERIMENTAL

The compound $\text{CF}_2\text{BrCFBrCl}$ was prepared by bromination of $\text{CF}_2=\text{CFCl}$ in a sealed tube. The ethylene was used in excess and allowed to boil off from the product, which was then used without further purification. The compounds $\text{CF}_2=\text{CFBr}$, $\text{CF}_2=\text{CFCl}$ and CF_3CFCl_2 were obtained from Peninsular Chemresearch, Inc.

The spectra were recorded on a Varian HR-60 spectrometer operating at 56.4 Mc/sec. The variable temperature probe insert has been described previously.⁷ The reported coupling constants are the averages taken from 10 to 15 spectra and were determined by the usual audio-frequency side-band technique.

RESULTS AND OBSERVATIONS

Bromotrifluoroethylene

The coupling constants of this compound have been reported previously.⁸ Since the relatively rigid geometry of the molecule precludes the existence of any rotational isomerism, the effect of solvents, if any, on the coupling constants in this molecule at constant temperature is then attributable solely to molecular interactions.

Table I shows the coupling constants of this compound determined in different solvents (50% by volume) and the percentage deviation of the coupling constants from that in the neat sample. The vicinal coupling constant J_{12} appears to have some correlation with the dipole moment⁹ of the solvent whereas with the geminal coupling constant J_{13} any such correlation is not obvious. However, it is noted that in some solvents the geminal J_{13} and the vicinal J_{12} differ by as much as 5% from the corresponding ones in the neat sample. The trans coupling constant J_{23} , however, remains essentially unaffected. The following trends are observable: the value of J_{12} in various solvents is never substantially larger than in the neat sample, whereas J_{13} is shifted in both directions by solvents; solvent molecules with highly polar or polarizable centers tend to cause more pronounced changes in the coupling constants; and finally, smaller solvent molecules tend to cause larger changes in the coupling constants. The solvents which are similar in nature to this olefin,

Table I Coupling constants of Bromotrifluoroethylene, cps.¹ (The values within brackets were determined at -105°C.)

Solvent	Dipole Moment Debye	J ₁₃	%Deviation from neat sample ²	J ₁₂	%Deviation from neat sample ²	J ₂₃	%Deviation from neat sample ²
CF ₂ =CFBr		73.74 (72.76)	0 0	56.58 (55.48)	0 0	122.83 (123.40)	0 0
S=C=S	0	71.70 (71.77)	-2.77 (-1.36)	56.42 (55.37)	-0.28 (-0.20)	123.11 (123.44)	+0.23 (0.00)
CF ₂ BrCF ₂ Br	~0.2	73.30	-0.60	56.50	-0.14	123.17	+0.28
CF ₂ ClCFCl ₂	~0.3	73.64	-0.14	56.69	+0.19	123.18	+0.28
CFCl ₃	0.45	73.26 (72.09)	-0.65 (-0.92)	56.84 (55.32)	+0.46 (-0.29)	123.38 (123.22)	-0.37 (-0.15)
dioxane	0.45	73.78	+0.05	55.08	-2.65	122.61	-0.18
CH ₃ CSCH ₃		74.26	+0.71	53.69	-5.11	122.46	-0.29
CH ₃ COOH	0.8	74.31	+0.77	55.98	-1.06	122.73	-0.08
(CH ₃ CH ₂) ₂ O	1.20	73.84 (73.84)	+0.14 (+1.48)	55.99 (53.04)	-1.04 (-4.40)	123.10 (123.09)	+0.22 (-0.25)
OSCl ₂	1.38	72.05	-2.29	55.82	-1.34	122.42	-0.33
CH ₃ OH	1.61	74.47	+0.99	55.74	-1.48	122.86	+0.02
CH ₃ CH ₂ OH	1.63	73.90 (73.86)	+0.22 (+1.51)	55.86 (53.85)	-1.27 (-2.94)	122.89 (123.12)	+0.05 (-0.23)
CH ₂ =CHCH ₂ Cl	2.0	73.08	-0.90	56.10	-0.85	122.99	+0.13
CH ₃ CHO	2.49	74.23	+0.66	55.10	-2.62	122.55	-0.23

Table I (continued)

Solvent	Dipole Moment Debye	J_{13}	%Deviation from neat sample ²	J_{12}	%Deviation from neat sample ²	J_{23}	%Deviation from neat sample ²
		(74.11)	(+1.86)	(53.54)	(-3.50)	(123.18)	(-0.18)
CH_3COCH_3	2.70	74.88	+1.55	54.85	-3.06	122.47	-0.29
$(\text{CH}_3\text{CO})_2\text{O}$	2.70	74.39	+0.88	55.40	-2.09	-122.60	-0.18
CH_3CN	4.0	74.61	+1.18	54.86	-3.04	-121.93	-0.73

1. Most probable errors are less than ± 0.10 cps.
2. The most probable errors are $\pm 0.14\%$ in J_{13} , $\pm 0.18\%$ in J_{12} , and $\pm 0.08\%$ in J_{23} .

namely, the halogenated ethanes and "Freon 11" (CFCl_3), do not cause large changes in the coupling constants.

At -105°C the coupling constants in the neat sample are noticeably different from those at room temperature (20°C). At this low temperature, as shown in Table I, the coupling constants of this compound also vary from solvent to solvent, and the differences in the coupling constants follow the same trends as at room temperature. However, the differences in the coupling constants between those determined in the solvents and those in the neat sample are enhanced at this low temperature. It is interesting to note that in those solvents which cause large changes from the neat sample, the geminal coupling constant J_{13} does not seem to be temperature dependent whereas the vicinal one J_{12} is strongly temperature dependent. It must be emphasized that as the differences in the coupling constants are sizeable, amounting to as much as 3 cps, they are well outside of experimental errors.

1,1-dichlorotetrafluoroethane

Since this compound has the CF_3 unit with three-fold symmetry, all three rotamers have equal population at all temperatures and hence any temperature dependence of the coupling constant cannot be the result of change in the equilibrium populations of the three rotamers. Brey and Ramey³ have reported the temperature dependence of the coupling constant of this compound. In this work the coupling constant has been determined in a number of solvents (50% by volume) at two temperatures.

Table II shows the coupling constants determined in different solvents and the percentage deviation of the coupling constants from that in the neat sample. The coupling constants determined in the solvents are invariably larger than that in the neat sample at both the temperatures. The coupling constants determined at the lower temperature (-60°C) are invariably larger than those determined at the higher temperature (20°C). In the solvent $\text{CF}_2\text{ClCFCl}_2$, which is similar to the solute, the coupling constant is identical with that in the neat sample.

Table II. Coupling Constants of CF_3CFCl_2 , in cps¹

Solvent	$J_{(20^\circ\text{C})}$	%Deviation from neat sample ²	$J_{(-60^\circ\text{C})}$	%Deviation from neat sample ²
CF_3CFCl_2 (neat)	5.73	0	5.97	0
$\text{CF}_2\text{ClCFCl}_2$	5.76	+0.52		
CFCl_3	5.81	+1.40	6.20	+3.85
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	5.84	+1.92	6.18	+3.52
CH_3CHO	5.85	+2.09	6.15	+3.02
CH_3OCH_3	5.89	+2.79	6.24	+4.52
CH_3OH	5.91	+3.14	6.21	+4.02
CH_3COCH_3	5.92	+3.32	6.24	+4.52

¹ All values are accurate to better than ± 0.10 cps.

² The deviation due to errors is less than $\pm 1.74\%$ for $J_{(20^\circ\text{C})}$ and $\pm 1.68\%$ for $J_{(-60^\circ\text{C})}$.

1,1,2-trifluoro-1,2-dibromo-2-chloroethane

At room temperature this compound exhibits an ABX spectrum.

The coupling constants have been determined in different solvents (90% solvent by volume) as well as in different concentrations of solution with acetone as the solvent. Table III lists the coupling constants determined in the different solvents and their percentage deviation from those in the neat sample. Table IV shows the coupling constants determined in different concentrations of acetone. Fig. 1 shows the geminal coupling constant, J_{AB} , as a function of the solvent concentration.

It is shown in Table III that the geminal coupling constant J_{AB} varies substantially in the different solvents. Evidently, this coupling constant increases with the dipole moment of the solvent. Solvents, like 1,4-dioxane and CH_3COOH , with relatively low molecular dipole moments but large "local" dipole moments, can cause as much change in the coupling constant as the more polar solvents. However, in the case of the sum $(J_{AX} + J_{BX})$ the differences in the values determined in the various solvents are small.

The data in Table IV shows strikingly the effect of solvent on coupling constant. J_{AB} becomes larger as the solvent concentration increases. There is a change of 5 cps in J_{AB} in going from the neat sample to the dilute solution of 6.2 mole percent in $\text{CF}_2\text{BrCFBrCl}$. Figure 1 shows that the change in J_{AB} is more gradual in the more concentrated solutions (50-100 mole percent in $\text{CF}_2\text{BrCFBrCl}$), and as the solution becomes more dilute, J_{AB} changes linearly with the concentration of solution. However, it is observed that the sum $(J_{AX} + J_{BX})$ varies only slightly as the concentration is varied.

Table III Coupling Constants of $\text{CF}_2\text{BrCFBrCl}$, cps.¹

Solvent	Dipole Moment Debye	J_{AB}	%Deviation from neat sample ²	$J_{AX} + J_{BX}$	%Deviation from neat sample ²
CS_2	0	165.00	-0.99	28.37	-2.68
$\text{CF}_2\text{BrCFBrCl}$	~0.3	166.64	0	27.63	0
$(\text{CH}_3\text{CH}_2)_2\text{O}$	1.20	169.26	+1.57	27.62	-0.04
CH_3COOH	0.8	169.68	+1.82	27.77	+0.51
$\text{CH}_3\text{CH}_2\text{OH}$	1.63	169.75	+1.87	27.74	+0.42
1,4-dioxane	0.45	170.67	+2.42	28.05	+1.52
$(\text{CH}_3\text{CO})_2\text{O}$	2.70	170.68	+2.42	27.93	+1.09
CH_3OH	1.61	170.87	+2.54	27.59	-0.14
CH_3CN	4.0	171.23	+2.76	27.78	+0.54
CH_3COCH_3	2.70	171.51	+2.92	27.79	+0.58

¹The most probable errors are ± 0.10 cps.

²The most probable errors are $\pm 0.06\%$ in J_{AB} and $\pm 0.37\%$ in $(J_{AX} + J_{BX})$.

Table IV Coupling Constants of $\text{CF}_2\text{BrCFBrCl}$
in Acetone Solutions, cps.¹

Concentration of $\text{CF}_2\text{BrCFBrCl}$		J_{AB}	%Deviation from neat sample ²	$(J_{AX} + J_{BX})$	%Deviation from neat sample ²
by volume	mole fraction				
10%	0.06	171.52	2.93	27.79	0.58
20%	0.13	171.12	2.69	27.84	0.76
30%	0.21	170.67	2.42	27.81	0.65
40%	0.28	170.16	2.11	27.84	0.76
50%	0.37	169.68	1.82	27.79	0.58
60%	0.47	169.03	1.44	27.82	0.69
70%	0.58	168.46	1.09	27.81	0.65
80%	0.71	167.79	0.69	27.77	0.51
90%	0.84	167.26	0.37	27.76	0.47
100%	1.00	166.64	0	27.63	0

¹The most probable errors are ± 0.10 cps.

²The most probable errors are $\pm 0.06\%$ in J_{AB} , and $\pm 0.37\%$ in $(J_{AX} + J_{BX})$.

The low temperature NMR spectrum of this compound is a superposition of the ABX spectrum of each of the three rotamers. The spectrum at -123°C has been assigned.² The coupling constants of the two more abundant rotamers have been determined in four solvents at -123°C , and the results are shown in Table V.

Examination of Table V shows that the coupling constants of the two rotamers do vary with the solvents at temperatures at which the rotamers were "frozen out". Rotamer I, which corresponds to the most abundant rotamer, shows for J_{AB} a high value in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$. The difference between these two values is 1.5 cps, a magnitude which is well beyond experimental error. For the same rotamer ($J_{AX} + J_{BX}$), determined in cis-2-butene, is noticeably different from the other three values. Rotamer II shows slightly different values of the coupling constant in the different solvents. The differences between these values may be small but not negligible.

Table V. Coupling Constants of the Rotamers
of $\text{CF}_2\text{BrCFBrCl}$ at -123°C^1

Solvent	Rotamer I		Rotamer II
	J_{AB}	$J_{AX} + J_{BX}$	$1/2 (J_{AX} + J_{BX})$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	169.15	-26.32	-13.26
$\text{CH}_3\text{CH}_2\text{Cl}$	170.61	-26.58	-13.58
CFCl_3	170.0	-26.60	-13.97
cis-2-butene	170.23	-25.53	-13.26

¹ J_{AB} is accurate to better than ± 0.4 cps, and the two sums ($J_{AX} + J_{BX}$) are accurate to better than ± 0.25 cps. The most probable errors in all cases are better than ± 0.1 cps.

DISCUSSION

The results on the three compounds studied indicate that fluorine coupling constants are solvent dependent. The effect of solvents on coupling constants can be quite pronounced if the solute and solvent molecules differ substantially in structure and have highly polar or polarizable centers. One might expect such solvent dependence due to molecular associations, which induce changes in the electron distribution in the molecules. It is expected that such changes in the electronic distribution should alter the contributions to the coupling constant from both through-bonds and through-space terms. One would expect that the latter term would be more susceptible to weak intermolecular interactions. It is noted that the solvent dependence of coupling constants is of the same order of magnitude as the observed temperature dependence of coupling constants reported in this paper and reported by Brey and Ramey.⁴

In the compound Bromotrifluoroethylene one can readily explain the fact that J_{23} is relatively independent of solvents whereas the other two coupling constants are dependent on the solvent by postulating that a large fraction of the J_{12} and J_{13} arise from the through-space mechanism whereas J_{23} arises almost entirely from the through-bond mechanism. It might be postulated that the polar centers of the solvent molecules interact with the non-bonding electron densities directly between the atoms F_1 and F_2 and between the atoms F_1 and F_3 , either aiding in relaying nuclear spin information across or hindering the transmission of same. The size and geometry of the solvent molecule certainly determine how close it can approach the solute molecule,

thereby determining the extent of the interaction. It is to be noted that with some solvents, particularly those solvent molecules which are similar to the solute molecules, the molecular interaction would be similar to that inherent in the neat sample. In this case no significant changes in the coupling constants would be observable as is the case. At lower temperatures the probability of weak molecular interactions would be enhanced whereas the probability of strong molecular interactions would always be high and would not be as temperature sensitive. The enhancement of the probability of weak molecular interactions would be accompanied by changes in the coupling constants. Precisely this behavior was observed in Bromotrifluoroethylene where the geminal J_{13} shows no temperature dependence in solvents which would be expected to associate strongly with the solute. It is probable that most every solute molecule is strongly associated with the solvent molecules at any reasonable temperature; therefore, there is very little temperature dependence of the molecular association and hence the temperature dependence of coupling parameters is entirely due to vibrational excitation. Since J_{13} shows little or no temperature dependence in these solvents it can be stated that the geminal coupling constant is not affected strongly by excitation of low lying vibrational modes. Having shown, thus, that J_{13} is not affected by excitation of low lying vibrational modes, the large temperature dependence of J_{13} in two cases in the neat sample and in the solvent CFCl_3 must come about as a result of temperature dependent molecular associations. In the case of the vicinal J_{12} , there is obviously a contribution from both factors vibrational excitation and molecular association.

It might be expected that the geminal J_{13} and the trans J_{23} have little dependence on excitation of vibrational modes. In the case of J_{13} the CF_2 end of the molecule should not vary much with excitation of the low lying vibrational modes. Likewise, if J_{23} comes about through the π -bonding, this might not be affected much by population of the torsional mode. On the other hand, a good deal of the vicinal J_{12} must come about through non-bonded interactions ("through space" coupling) and this would depend strongly upon the excitation of the torsional mode, as observed.

The results on $\text{CF}_2\text{BrCFBrCl}$ show strikingly the effect of varying degrees of molecular association on coupling constant. The more polar solvents would effect stronger molecular associations as would solvents with more than one polar center. If the solvent is more polar than the solute, it is expected that solute-solvent interaction would be more effective than solute-solute interaction in changing the coupling constant. Hence in such a solution it is expected that in the more concentrated solutions the change in the coupling constant with the concentration of solution would be more gradual than in the dilute solutions, as observed in the data for J_{AB} determined in the acetone solutions. The same type of argument also explains why in the solvent CS_2 , which is less polar than the solute, the value for J_{AB} is less than that in the neat sample. It is probable that in a non-polar solvent in which the ratio of solvent to solute molecules is high, i.e. dilute solution, the solute molecule is relatively "free".

CONCLUSION

This study of the effect of solvents on the coupling constants of three compounds, $\text{CF}_2=\text{CFBr}$, CF_3CFCl_2 , and $\text{CF}_2\text{BrCFBrCl}$, shows that the coupling constants vary with the solvents. This implies that intermolecular interactions affect fluorine coupling constants to a degree that is not negligible. This effect of molecular interactions on coupling constants may be due to the dipolar character and polarizability of the interacting molecules. The interactions appear to be essentially the same kind, and detailed differences arise from the nature and dipolar character of the solvent molecules.

The results of this study, in conjunction with the results of Brey and Ramey show the magnitude of the error which can be made when one assumes that the observed temperature dependence of coupling constants of compounds, substituted ethanes in particular, arise solely from changes in the equilibrium populations of the rotamers. This study demonstrates that the temperature dependence of coupling constants for a given isomer may in large part come about as the result of temperature dependent molecular association as well as population of excited vibrational states.

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FIGURE CAPTION

Fig. 1. The geminal coupling constant J_{AB} of $CF_2BrCFBrCl$ as a function of concentration in acetone solution.

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