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R. A. Newmark and C. H. Sederholm

September 1963

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ABSTRACT

The spectrum of $\text{CF}_2\text{BrCFBrCl}$ has been redetermined at 150°K in CFCl_3 as a solvent. The coupling constants, chemical shifts, and relative energies of the three rotamers have been determined with considerable care. Assuming that high temperature coupling constants and chemical shifts are time-weighted averages of the coupling constants and chemical shifts of the individual rotamers, these quantities have been calculated for several high temperatures, and compared with the experimental values, which have been determined in the same solvent.

All of the spectra involved are typical AEX spectra. The experimental value for $1/2(J_{\text{AX}} + J_{\text{BX}})_{\text{AVE}}$ is 0.6 to 1.3 cps lower than the calculated value. Excellent agreement is obtained between the calculated and observed chemical shift between the A and B fluorine atoms. At 371°K there is a large difference between the calculated and observed chemical shifts between any other pair of fluorine nuclei, including the solvent nuclei. This difference decreases linearly with temperature and extrapolates to 0 at approximately the temperature of the low temperature data. The cause of these discrepancies is discussed.

INTRODUCTION

In the paper by Gutowsky and Saika¹ it was pointed out that quantities, such as coupling constants and chemical shifts, which are observed in systems undergoing fast chemical exchange should be time-weighted averages of those quantities for each of the various species that is undergoing transformation. In the case of substituted ethane molecules in particular, the high temperature coupling constants and chemical shifts have been assumed to be weighted averages of the coupling constants and chemical shifts for the three individual rotamers. Indeed, Gutowsky, Belford, and McMahon² have attempted to calculate the chemical shifts and coupling constants for the three rotamers by least squares fitting of the observed high temperature coupling constants and chemical shifts as a function of temperature. They did such curve fitting on $\text{CF}_2\text{Br}-\text{CFBrCl}$.

Recently, Brey and Ramey³ have succeeded in recording a low temperature spectrum of the above compound in which the spectra of the three rotamers are resolved. The low temperature coupling constants which they reported were not close to those obtained by Gutowsky, Belford, and McMahon. Brey and Ramey explained this difference by pointing out that the coupling constants and chemical shifts connected with a single rotamer are indeed temperature dependent since as the temperature is raised, the higher rotational levels will be populated which will give a larger weight to the angles not corresponding to the staggered configuration. This explanation has been used previously several times to explain, for instance, the temperature dependence of the F-F coupling constant in $\text{CF}_3 - \text{CF}(\text{NO}_2) - \text{CF}_2\text{NO}_2$.⁴

It is somewhat difficult to understand how the above consideration can

have a large effect. If the potential energy as a function of dihedral angle is symmetric about that angle corresponding to the staggered configuration, constant and linear terms in the coupling constant or chemical shift vs. dihedral angle will result in no temperature dependence of the averaged coupling constant or chemical shift. It is fairly difficult to imagine a large term of second order or higher in the dihedral angle. As a result of the above considerations, it was thought desirable to look into both sets of data more carefully and see how precisely high temperature coupling constants and chemical shifts are predicted from the low temperature data with the following assumptions.

A coupling constant or chemical shift at high temperatures should be given by:

$$(F^i)_{\text{AVE}} = X_I F_I^i + X_{II} F_{II}^i + X_{III} F_{III}^i \quad (1)$$

where the subscripts refer to the three rotamers, X_k is the mole fraction of the k^{th} rotamer, and F_k^i is the i^{th} chemical shift or coupling constant of the k^{th} rotamer. The ratio of the X's is given by:

$$X_I : X_{II} : X_{III} = Q_I' : Q_{II}' e^{-\Delta E_{II}/RT} : Q_{III}' e^{-\Delta E_{III}/RT} \quad (2)$$

where Q_I' is the partition function, excluding the torsional vibration, for the i^{th} rotamer, and ΔE_i is the difference in energy between the potential minimum of rotamer I and rotamer i . If we assume, as seems reasonable, that the low lying vibrational frequencies of the three rotamers are the same to within 10%, we make only a few percent error by setting $Q_I' = Q_{II}' = Q_{III}'$.

Then:

$$X_I : X_{II} : X_{III} = 1 : e^{-\Delta E_{II}/RT} : e^{-\Delta E_{III}/RT} \quad (3)$$

$$(F^i)_{\text{AVE}} = (F_I^i + e^{-\Delta E_{\text{II}}/RT} F_{\text{II}}^i + e^{-\Delta E_{\text{III}}/RT} F_{\text{III}}^i) / (1 + e^{-\Delta E_{\text{II}}/RT} + e^{-\Delta E_{\text{III}}/RT}) \quad (4)$$

EXPERIMENTAL

$\text{CF}_2\text{BrCFBrCl}$ was prepared by bromination of $\text{CF}_2 = \text{CFCl}$ (Peninsular Chem-research Inc.) 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. All peaks in the NMR spectrum were directly attributable to the product.

Experiments performed in this laboratory earlier have shown that the coupling constants in $\text{CF}_2\text{BrCFBrCl}$ are a function of the solvent employed. Hence all measurements were made on a 50 volume percent solution of $\text{CF}_2\text{BrCFBrCl}$ in CFCl_3 .

Spectra were taken at various temperatures between 150°K and 371°K. The spectra were recorded on a Varian HR-60 spectrometer operating at 56.4 Mc/sec. equipped with a flux-stabilizer and integrator. The variable temperature insert used has been described previously.⁵ The temperatures reported are accurate to $\pm 3^\circ$. Chemical shifts and coupling constants were determined by the usual audio sideband technique. Two modulation frequencies were used to determine the $\text{CFCl}_3 - \text{CF}_3\text{Br}$ chemical shift; one at about 1000 cps and the second at 10 cps to calibrate the spectrum. All reported numbers are averages taken over many spectra. Low temperature areas were determined using the Varian Integrator. Chemical shifts and coupling constants are tabulated in Table I. The observed low temperature spectrum is shown in Fig. 1.

RESULTS

The low temperature spectrum consists of 24 peaks (see Fig. 1). From

peak separations and intensities, peaks 1-6, 10-11, and 16-18 are assigned to an ABX spectrum of rotamer I. Only 11 peaks of this ABX spectrum are observed since, using Pople's notation,⁶ D_+ is almost equal to D_- . Peaks 9, 12-15, and 22-24 correspond to eight of the eleven possible peaks of the ABX spectrum for rotamer II. Only one peak of the two outer doublets could be resolved. The other three are near peak 8 and peaks 15-17. We are left with peaks 7-8 and 18-21, which are essentially an A_2X spectrum for rotamer II. Because of the accidental near degeneracy of the chemical shifts for the magnetically non-equivalent AB fluorine atoms in rotamer II, it is only possible to obtain $\frac{1}{2}(J_{AX} + J_{BX})$. On the basis of this assignment the relative areas at 150°K for the three rotamers are 69.84 ± 0.5 ; 24.45 ± 0.5 ; 5.71 ± 0.2 . Our assignment differs from that of Brey and Ramey³ in that we are unable to find the four peaks they attributed to the AB part of rotamer II. They did not assign the doublet, peaks 7-8, to any of the rotamers but presumably assumed it to be an impurity.

Double resonance experiments using the Varian integrator confirm the above assignment. Peaks 7-8 collapse when peaks 19-21 are irradiated. Peaks 5-6 collapse when lines 17-18 are irradiated and peaks 3-4 collapse when lines 16-17 are irradiated. This pattern of collapse shows J_{AX} and J_{BX} are opposite in sign to J_{AB} for rotamer I.⁷ Double irradiation of the room temperature spectrum leads to the same conclusions for the signs of the averaged coupling constants.

As the temperature is increased the spectrum coalesces into two peaks at about the locations of 3-7 and 16-18; at temperatures above 229°K the exchange rate is sufficiently fast that a time averaged ABX spectrum is obtained. The coupling constants were accurately determined at four temperatures where

exchange is rapid and these are also given in Table I.

The integrated areas of the low temperature peaks are proportional to the number of fluorine nuclei absorbing. Therefore the relative population of the three rotamers, and hence the relative energies of the potential minima, can be determined from the integrated areas at 150°K. The energies so determined are $E_I = 0$ cal/mole, $E_{II} = 313 \pm 10$ cal/mole, and $E_{III} = 746 \pm 30$ cal/mole.

Dipole moment and steric considerations lead to the following assignment of the relative stability of the rotamers (see Fig. 2). Rotamer I corresponds to drawing A, rotamer II corresponds to drawing B, and rotamer III corresponds to drawing C. This assignment is supported by the chemical shifts . . . in rotamers I and II F_X is gauche to a fluorine and a bromine atom, and ν_X in these rotamers is almost the same. However, this assignment, while interesting, is not necessary for the discussion to follow.

Chemical Shifts

$(\nu_A - \nu_B)_{II}$ is so small that it is not observable in our spectra. However, an upper limit of about ± 30 cps can be put upon it from the width of the unresolved lines. Assuming that Eq. (1) is valid to plus or minus 40 cps requires that $(\nu_A - \nu_B)_{III}$ is negative, arbitrarily taking $(\nu_A - \nu_B)_I$ as positive. It is now possible to calculate $(\nu_A - \nu_B)_{II}$ at the four different elevated temperatures. If the calculated values turn out to be the same for these four temperatures, and within the known limits, one can conclude with reasonable certainty that Eq. (4) holds for this quantity and that the calculated value is close to the true value. This calculation was made and the resulting calculated values of $(\nu_A - \nu_B)_{II}$ are: -9.7, -12.3, -11.6, and -10.3 at 242, 300, 322 and 371°K respectively. Using the average, -11.0, to calculate $(\nu_A - \nu_B)_{AVE}$ at the higher temperatures gives the results tabulated in Table II, which are

almost within the experimental uncertainty in the high temperature values. No values more than a few cycles different from -11.0 would yield a reasonable fit to the data over the 130° temperature range. The close agreement between the four calculated values leads one to believe that Eq. (4) is obeyed very well for $\nu_A - \nu_B$.

Using the above average value for $(\nu_A - \nu_B)_{II}$, the chemical shifts of the three nuclei from an internal standard, CFCl_3 , were determined for each rotamer. These are listed in Table I. From the low temperature data, the high temperature values of $(\nu_A)_{\text{AVE}} - \nu_{\text{CFCl}_3}$, $(\nu_B)_{\text{AVE}} - \nu_{\text{CFCl}_3}$, $(\nu_X)_{\text{AVE}} - \nu_{\text{CFCl}_3}$, and $(\nu_X - \nu_{AB})_{\text{AVE}}$ can be calculated using Eq. (1). It is seen in Table II that the calculated values differ appreciably from the experimental values, implying that the chemical shifts are temperature dependent. The differences between the calculated values and the experimental values are plotted in Fig. 3. It is seen that this difference extrapolates to zero at about 150°K as would be expected. This lack of agreement is attributable to two phenomena: (1) the excitation of torsional modes, or (2) temperature dependent intermolecular associations. It is somewhat surprising that Eq. (1) holds extremely well for the quantity $\nu_A - \nu_B$ over a wide temperature range, but does not hold for any other pair of chemical shifts. This fact is consistent with explanation (2) above, but not with explanation (1). The excitation of torsional vibrational modes should affect $\nu_A - \nu_B$ just as drastically as any other pair of chemical shifts. However, nuclei A and B are nearly equivalent chemically. Hence they are going to feel nearly the same perturbation of the magnetic field due to intermolecular associations. However, the perturbation at the X nucleus will be quite different, and likewise at the CFCl_3 fluorine nucleus. Hence, explanation (2) above, would predict the observed behavior.

In support of this explanation, the chemical shift between two fluorinated methanes, CFCl_3 and CF_3Br (mixed in equal proportions) varies linearly with temperature, changing 31 cps in 150° . These results are plotted in Fig. 4.

Coupling Constants

Only $\frac{1}{2}(J_{\text{AX}} + J_{\text{BX}})$ can be accurately determined experimentally due to the degeneracies in the spectra. The low temperature values of this function for the three rotamers are listed in Table I. The high temperature experimental and calculated values are listed in Tables I and II. Again, the relative signs have been chosen to make Eq. (1) hold as well as possible.

It is seen that at high temperatures, $\frac{1}{2}(J_{\text{AX}} + J_{\text{BX}})_{\text{AVE}}$ determined experimentally, is approximately constant over the temperature range; the calculated value, however, is 0.6 to 1.3 cps higher. This discrepancy is attributable to either population of excited torsional states or temperature dependent intermolecular associations. Schug, McMahon, and Gutowsky⁸ have investigated the first phenomenon for vicinal proton coupling constants. At present, work is in progress in this laboratory to investigate the second effect.

CONCLUSIONS

In $\text{CF}_2\text{Br-CFBrCl}$, high temperature coupling constants and chemical shifts can be fairly accurately calculated from the low temperature values of the quantities in the individual rotamers. An error on the order of 10% in the calculated, high temperature coupling constants is attributable to either population of excited torsional states or temperature dependent molecular association. The latter can cause a much larger variation between calculated and observed chemical shifts when the effect does not cancel out. These results on one molecule, would tend to make low temperature coupling constants

and chemical shifts calculated from high temperature curve fitting somewhat questionable. However, high temperature coupling constants and chemical shifts calculated from low temperature data seem to be accurate to within 10-20%.

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Table I. Experimental chemical shifts and coupling constants of the three rotamers (I, II and III) of $\text{CF}_2\text{BrCFBrCl}$ at 150°K , and of the averaged spectrum at higher temperatures. $\nu_{AB} = \frac{1}{2}(\nu_A + \nu_B)$; chemical shifts are measured from the solvent, CFCl_3 . All values in cps.^a

	J_{AX}	J_{BX}	$\frac{1}{2}(J_{AX} + J_{BX})$	J_{AB}	$\nu_A - \nu_B$	$\nu_X - \nu_{AB}$	ν_A	ν_B	ν_X
I	-11.8	-14.8	-13.3	170.0	244.6	605.3	3438.8	3194.2	3921.8
II			-14.0		-11.0 ^b	500.2	3474.5	3485.4	3980.2
III	-20.3	-21.3	-20.8	160	-210.3	552.6	3639.9	3859.2	4297.6
242°K	-13.48	-14.42	-13.95	168.0	112.31	536.5	3450.6	3338.3	3930.0
300°	-13.40	-14.14	-13.77	167.26	94.57	522.7	3436.2	3341.6	3911.6
322°	-13.61	-14.07	-13.84	167.15	89.13	517.0	3429.9	3340.7	3902.3
371°	-13.44	-13.96	-13.70	167.13	80.22	507.6	3417.8	3337.6	3885.3

^a J_{AX} and J_{BX} are accurate to ± 0.25 cps at 150°K and 242° , ± 0.20 cps at 300° , and ± 0.15 cps at 322° and 371° . Except for rotamer III, J_{AB} is accurate to better than 0.4 cps. $\nu_A - \nu_B$ at 300° and above is accurate to ± 0.40 cps; all other chemical shifts have a standard deviation less than 0.5 cps.

^b This number is calculated using Eq. (1), see text.

Table II. Calculated chemical shifts and coupling constants at high temperatures using weighted averages of the low temperature data, and the deviations from the experimental quantities.

$\Delta X = X_{\text{cal'd}} - X_{\text{observed}}$. Chemical shifts are measured from the solvent, CFCl_3 , in cps.

	$\frac{1}{2}(J_{AX} + J_{BX})$	$\Delta \frac{1}{2}(J_{AX} + J_{BX})$	$\nu_A - \nu_B$	$\Delta(\nu_A - \nu_B)$
242°K	14.55	0.60	112.10	-0.21
300°	14.77	1.00	94.77	0.20
322°	14.84	1.00	89.55	0.42
371°	14.98	1.28	79.79	-0.43

	ν_A	$\Delta(\nu_A)$	ν_B	$\Delta(\nu_A)$	ν_X	$\Delta(\nu_X)$
242°K	3474.8	24.2	3362.7	24.4	3986.1	56.1
300°	3480.7	44.5	3385.9	44.3	3997.5	85.9
322°	3482.7	52.8	3393.2	52.5	4001.2	98.9
371°	3485.9	68.1	3406.1	68.5	4007.6	122.3

FIGURE CAPTIONS

- Fig. 1. The spectrum of $\text{CF}_2\text{BrCFBrCl}$ in CFCl_3 (50% solution by volume) at 150°K . The separation between peaks 1 and 24 is 1243 cps.
- Fig. 2. The three rotamers of $\text{CF}_2\text{BrCFBrCl}$.
- Fig. 3. The difference between the calculated chemical shifts, based on the results at 150°K , and the experimental chemical shifts observed at high temperatures.
- $\Delta Y = Y_{\text{cal d}} - Y_{\text{obs}}$, $Y = \nu_X, \nu_A, \nu_X - \nu_{AB}$, where $\nu_{AB} = \frac{1}{2}(\nu_A + \nu_B)$. The curve for $\Delta\nu_A$ is within experimental error of the one for $\Delta\nu_B$.
- Fig. 4. The chemical shift between CFCl_3 and CF_3Br as a function of temperature.

REFERENCES

1. H. S. Gutowsky and A. Saika, J. Chem. Phys. 21, 1688 (1953).
2. H. S. Gutowsky, G. G. Belford, and P. E. McMahon, J. Chem. Phys. 36, 3353 (1962).
3. W. S. Brey and K. C. Ramey, J. Chem. Phys. 39, 0000 (1963).
4. W. S. Brey, K. C. Ramey, and K. D. Lawson, private communication.
5. D. S. Thompson, R. A. Newmark, and C. H. Sederholm, J. Chem. Phys. 37, 411 (1962).
6. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance (McGraw-Hill Book Company, Inc., New York, (1959)), p. 132
7. J. D. Baldeschwieler and E. W. Randall, Chem. Rev. 63, 81 (1963).
8. J. C. Schug, P. E. McMahon, and H. S. Gutowsky, J. Chem. Phys. 33, 843 (1960).

Fig. 1

Fig. 2

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Fig. 3

Fig. 4

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