NUCLEAR SPIN RELAXATION IN BENZYL FLUORIDE : V– ^{19}F INTRA AND INTERMOLECULAR RELAXATION OF BENZYL FLUORIDE IN SOLUTION

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SUMMARY

^{19}F relaxation times of benzyl fluoride in acetone-d_6 and in methanol-d_4 were measured and extrapolated at infinitely dilute solution. The fluorine relaxes through intramolecular dipole-dipole (DDa) and spin-rotation (SR) mechanisms in acetone-d_6 ,and through DDa,SR and inter-molecular dipole-dipole mechanisms in methanol-d_4.The DDa contribution can be recalculated from the overall and internal reorientational motions through ^{2}D measurements on the same solutions.The separation of the different contributions are consistent with those made on the proton rela-xation times and correlates more closely with poor solvation of benzyl-fluoride in acetone-d_6 and with greater solvation in methanol-d_4.

INTRODUCTION

In previous papers III and IV [1] ,we studied by deuterium relaxation times,the overall and the internal reorientational motions of benzyl fluoride in two typically different solvents , a dipolar one ,acetone, and a protic one, methanol and by proton relaxation times [IV], the different contributions occuring,particularly the spin-rotation and the intermolecular dipole-dipole contributions .The aim of this paper is to study by fluorine relaxation to obtain precise information on the solute-solvent interactions through fluorine spin-rotation and intermolecular dipole-dipole mechanisms.

EXPERIMENTAL

The fluorine relaxation times measurements were made according to the procedure described in the experimental part of paper II [2] and the solutions were prepared as in paper IV.

RESULTS

T_1 relaxation times of the benzylic fluorine were measured using the inversion-recovery method [3], through the temperature interval from 313 to 200 K at four mole fractions of benzyl fluoride in acetone-d_6 : 1 , 0.51 ; 0.31 ; 0.15 (Table 1) and at four mole fractions of benzyl fluoride in methanol-d_4 : 1 , 0.36 ; 0.20 ; 0.09 (Table 2). In the last case, several other molar fractions were used at 303 K.

INTERPRETATION

(a) Theoretical expression of the different fluorine relaxation

mechanisms of benzyl fluoride in solution

Fluorine relaxation rates are the sum of several contributions related to different relaxation mechanisms : the intramolecular dipole-dipole interaction (proton-fluorine) R_{1a-FH}^{DD} the intermolecular dipole-dipole interactions R_{1r}^{DD} and the spin-rotation mechanism R_1^{SR}. The chemical shift anisotropy and the scalar coupling mechanisms are negligible at the working frequency as studied in analogous cases [4,5]
Therefore :

$$R_1 = R_{1a-FH}^{DD} + R_{1r}^{DD} + R_1^{SR} \qquad (1)$$

All the contributions are dependent on x, the mole fraction of the solute in the solution, through the appropriate correlation times, as was shown in paper III, according the expression

$$R_1^x = R_{1a-FH}^{DD\,x} + R_{1r}^{DDx} + R_1^{SRx} \qquad (2)$$

where R^x means the value of the appropriate contribution at mole fraction x.

The intermolecular dipole-dipole interaction in the solutions $C_7H_7F/$ solvent has two terms, the solute-solute and the solute-solvent interactions according with formula (3) :

$$R_{1r}^{DDx} = x \ (R_{1r-FF}^{DDx} + R_{1r-FH}^{DDx}) + (1-x) \ R_{1r-FD}^{DDx} \qquad (3)$$

TABLE 1

Observed benzylic fluorine relaxation times for benzyl fluoride in
acetone-d_6, at several temperatures [a,c]

T(K)	1 [b]	0.51 [b]	0.31 [b]	0.15 [b]
313	17.6	22	25	29
294	13.8	17.6	22	27
278	10.3	14.2	18.3	23
263	7.3	11.2	14.8	19.8
250	5.4	8.4	11.8	17.2
238	3.9	6.4	8.9	13.0
227	2.8	4.9	6.8	9.8
217	2.1	3.7	5.1	7.4
208	1.50	2.8	3.9	5.6
200	1.09	2.2	2.9	4.2

[a] Calculated from smooth curves through T_1 data points, in seconds.

[b] Mole fraction of benzyl fluoride in acetone-d_6

[c] Estimated errors on relaxation times $\pm$ 5 %.

TABLE 2

Observed benzylic fluorine relaxation times for benzyl fluoride in
methanol-d_4, at several temperatures [a,c]

T(K)	1 [b]	0.36 [b]	0.20 [b]	0.09 [b]
313	17.6	22	27	30
294	13.8	18.1	22	26
278	10.3	14.1	17.9	21
263	7.3	10.4	14.3	16.7
250	5.4	7.7	10.7	12.7
238	3.9	5.7	7.5	9.6
227	2.8	4.2	5.8	7.3
217	2.1	3.1	4.3	5.5
208	1.50	2.3	3.2	4.2
200	1.09	1.69	2.4	3.2

[a] Calculated from smooth curves through T_1 data points, in seconds.

[b] Mole fraction of benzyl fluoride in acetone-d_6

[c] Estimated errors on relaxation times $\pm$ 5 %.

where R^x_{1r-FF} is the intermolecular interaction of two fluorine nuclei in two solute molecules with d^o_{FF} as the distance of closest approach, a the radius of the molecule assumed as a sphere and τ^x_t as the translational correlation time :

$$R^{DDx}_{1r-FF} = \frac{6\pi\hbar^2 N}{a^2} \gamma^4_F d^{o-1}_{FF} \tau^x_t \tag{4}$$

and R^{DDx}_{1-rFX} is the intermolecular interaction of a fluorine nucleus and another nucleus (H or D) in two molecules with d^o_{FX} as the distance of closest approach :

$$R^{DDx}_{1r-FX} = \frac{16}{3} \frac{\pi\hbar^2 N}{a^2} \gamma^2_F \gamma^2_X I_X(I_X+1) d^{o-1}_{FX} \tau^x_t \tag{5}$$

The distances of closest approach of nuclei of two solute molecules d^o_{FF} or d^o_{FH} are considered to be equal but the distance of closest approach of nuclei between solute and solvent molecules d^o_{FD} is different from d^o_{FF} and d^o_{FH}. Taking into account the values of γ_H, γ_F, I_H in formula (5), we can reduce formula (3) to the following one :

$$R^{DDx}_{1r} = 1.19 \text{ x } R^{DDx}_{1r-FH} + (1-x) R^{DDx}_{1r-FD} \tag{6}$$

The total fluorine relaxation rate has the following empirical form :

$$R^x_1 = R^{DDx}_{1a-FH} + 1.19 \text{ x } R^{DDx}_{1r-FH} + (1-x) R^{DDx}_{1r-FD} + R^{SRx}_1 \tag{7}$$

For a quantitative treatment, we interpret only the relaxation rates extrapolated at infinitely dilute solution :

$$R^o_1 = R^{DDo}_{1a-FH} + R^{DDo}_{1r-FD} + R^{SRo}_1 \tag{8}$$

where R^o means the value for the appropriate contribution at infinitely dilute solution. For the effective separation of these three contributions we have evaluated the intramolecular relaxation and the temperature dependence of the spin-rotation.

The fluorine intramolecular dipole-dipole relaxation is determined by two heteronuclear interactions in the benzylic group and two heteronuclear interactions with the ortho protons. In this last case, the corresponding distance is evaluated through the mean $2 < r^{-6}_{FHo} > = r^{-6}_{max} + r^{-6}_{min}$
The corresponding formula is :

$$R^{DD}_{1a-FH} = 2\hbar^2\gamma^2_F\gamma^2_H \{r^{-6}_{FH} f(\Omega_{HF}, D_{iso}, R_{int}) + < r^{-6}_{FHo} > \frac{1}{2R_{int}}\} \tag{9}$$

where $f(\Omega, D_{iso}, R_{int})$ describe the influence of the motions : the overall motion characterized by the diffusion constant D_{iso}, the internal rota-

tional motion of the benzylic group characterized by the internal diffusion constant R_{int} about the aromatic-benzylic bond (X axis) and the orientation between the dipole-dipole vector $\overrightarrow{FH}$ and the X axis (angle θ). Following Woessner this function is :

$$f(\Omega,D_{iso},R_{int}) = \frac{1/4(3\cos^2\theta-1)^2}{6D_{iso}} + \frac{3\sin^2\theta\cos^2\theta}{6D_{iso}+R_{int}} + \frac{3/4\sin^4\theta}{6D_{iso}+4R_{int}} \quad (10)$$

where the function describing the influence of orientation and motion of the dipole-dipole vector $\overrightarrow{FH}_o$ is $<r_{FHo}^{-6}> \frac{1}{2R_{int}}$. The values of the relevant distances and angles are [6] :

$$r_{FH} \simeq 2.01 \ \overset{o}{A}, \ <r_{FH}_o> = 2.83 \ \overset{o}{A}, \ \theta = 86°41'$$

Therefore

$$R_{1a-FH}^{DD} = 1.55 \ 10^{10} \ f(\Omega,D_{iso},R_{int}) + 5.05 \ 10^8/R_{int} \quad (11)$$

The spin-rotation has the following expression for the rotation of a spherical molecule [7]

$$R_1^{SR} = 2I \ kT \ C_0^2 \ \hbar^{-2} \ \tau_{SR} \quad (12)$$

where C_0 is the spin-rotational coupling constant of fluorine and τ_{SR} is the spin-rotation correlation time related according Hubbard [7] as to the rotational correlation time :

$$\tau_{SR}\tau_c = \frac{I}{6kT} \quad (13)$$

These two formula are used to predict the temperature dependence of the spin-rotation. For a nucleus localised in a group with internal rotation within a molecule, the spin-rotation relaxation rate is the sum of two terms :

$$R_1^{SR} = f_{SR}(I_o, \ C_o) \ \tau_{SRO} + g_{SR} \ (I_\alpha, \ I_{\alpha\alpha}, \ C_\alpha) \ \tau_{SR\alpha} \quad (14)$$

where I,C and τ_{SR} are the inertia moment, the spin-rotation coupling constant and the spin-rotation correlation time, respectively of the overall molecule and of the group with internal rotation [8,9] along the appropriate axis.

(b) Relaxation rates of benzylic in acetone-d_6

For all temperature, the plot of R_{1a}^x versus x is linear. The extrapolation to infinitely dilute solution gives R_1^o.

The plot of R_1^o versus 1/T gives straight lines only for temperatures less than 250 K. It means from formula (2) and (8) that spin-rotation occurs. From the differences of the observed relaxation rates at T>250 K

and of the extrapolated straight line from the low temperatures region, the spin-rotation times are calculated and shown on Table 3. This contribution is higher than that observed from proton measurements (paper IV). The spin-rotation coupling constant calculated according formula (12) and (13) gives $(\overline{C}_0{}^2)^{1/2}$ = 8 kHz $\pm$ 1, quite close to that observed in the isotopic solution (paper II) and higher than that observed for the proton in the same solvent (paper IV). It is generally known that the fluorine spin-rotation is more important than that of the hydrogen [4,10]

The intramolecular dipole-dipole fluorine relaxation time is calculated from formula (11) with the diffusion constant already measured from deuterium measurements of the perdeuterated compound in the same solvent (paper III). The values are shown on Table 3. The calculated intramolecular interaction and the observed relaxation rate without the spin-rotation relaxation rate are in good agreement. We can conclude that the third term in formula (8) is negligible , i.e the solute-solvent intermolecular interaction is quite small, describing a poor solvatation of benzyl fluoride in acetone.

The calculated and experimental NOE measurements extrapolated at infinite dilution in this A $\{X_2\}$ system are in good agreement. The fractional enhancement of the magnetization of the fluorine when the proton are saturated noted $f_F^o(H)$ is 0.28 (extrapolation at infinite dilution) (Table 4). The theoretical value ($f_F^o(H)$ = $\frac{\gamma_F}{2\gamma_H}\frac{R^o{}_{1a-FHo}}{R_1^o}$), as the intramolecular relaxation rate determined by heteronuclear interactions is 0.30.

All the previous comments are made on values extrapolated at infinitely diluted solutions. Some comments on the effect of dilution on relaxation times can be made through ^{13}C relaxation times (Table 5) on pure benzyl fluoride and on a solution in acetone (molar ratio 0.73 and measures at 303 K). The NOE are also determined. The quaternary carbon relaxation time is very high. The para carbon at several working frequencies cannot be measured because of overlap. The other carbon relaxation times and the corresponding NOE are almost the same for the two liquids, except for the benzylic carbon (higher value of relaxation time and lower values of NOE than the previous carbons when dilution occurs). So the ^{13}C relaxation rates contributions are almost only from intramolecular dipole-dipole and spin-rotation interactions. The previous result means that, in solution the benzylic carbon relaxation rate has a higher contribution from spin-rotation than in the pure liquid. It seems that ^{13}C is clearly

TABLE 3

Intramolecular (DD) and spin-rotation relaxation rates of benzylic
fluorine for benzyl fluoride in acetone-d_6 at infinite dilution.

T(K)	T_1^O [a,b]	T_{1a-FH}^{DDo} [c]	T_1^{SRo} [a,b]
313	32	59	78
294	30	49	92
278	29	40	122
263	28	33	240
250	27	27	-
227	18	19	-
208	12.5	12.9	-
200	10.5	10.8	-

[a] Calculated from smooth curves at infinite dilution in seconds

[b] Estimated errors on relaxation times ± 10 %.

[c] Theoretical intramolecular dipole-dipole relaxation times.

TABLE 4

Observed Nuclear Overhauser Effect ($f_F^x(H)$) of benzyl fluorine in
acetone-d_6, at 303 K.

x [a]	1	0.73	0.51	0.31	0.15	0 [b]	0 [c]
$f_F^x(H)$	0.43	0.39	0.36	0.33	0.31	0.28	0.30

[b] NOE ($f_F^o(H)$) measurement extrapolated at infinite dilution

[c] Theoretical NOE at infinite dilution $f_F^o(H)$

[a] Molar fraction of benzyl fluoride in acetone-d_6.

sensitive to changes of the internal rotation motion of the benzylic
group (decreasing of the energy barrier with dilution) through spin-
rotation according to equation (14). The sensitivity through this
mechanism is greater than that of proton and fluorine , as the spin-rotation
was evaluated as negligible in this solvent.

(c) Relaxation rates of benzylic fluorine in methanol-d_4

Plots of benzylic fluorine relaxation rates versus x are curves for
all temperatures in contrast to the case of the acetonic-solution and as
for benzylic protons in methanol. The extrapolation to x → o can easily
give R_1^o and the corresponding fluorine relaxation times at infinitely
dilute solution T_1^o are shown on Table 6.

TABLE 5

Observed ^{13}C relaxation times and Nuclear Overhauser Effect $(f_C(H))$, for pure benzyl fluoride and for solution in acetone-d_6, at 303 K

Carbons	pure		.73 in acetone-d_6	
	T_1^a	$f_C(H)^b$	T_1^a	$f_C(H)^b$
C_1 (quaternary)	~ 97	–	–	–
C_2 (ortho)	17.4	1.71	17.3	1.72
C_3 (meta)	16.8	1.65	16.4	1.70
C_7 (benzylic)	17.4	1.43	16.9	1.51

[a]Estimated errors on relaxation times $\pm$ 10 %

[b]Estimated errors on Nuclear Overhauser Effect $\pm$ 0.15 %.

TABLE 6

Intra and intermolecular dipole-dipole and spin-rotation relaxation times of benzylic fluorine for benzyl fluoride in methanol-d_4 at infinite dilution

T(K)	T_1^{o} [a,b]	T_{1a-FH}^{DDo} [c]	T_{1r-FD}^{DDo} [a,b]	T_1^{SRo} [a,b]
313	36	68	152	145
294	32	53	117	230
278	27	41	92	450
263	22	32	72	–
250	17	25	55	–
227	10.3	15	33	–
208	6.1	9.3	18	–
200	4.9	7.3	15	–

[a]Calculated from smooth curves a infinite dilution, in seconds.

[b]Estimated errors on relaxation times $\pm$ 10 %

[c]Theoretical intramolecular dipole-dipole relaxation times.

Plots of the logarithm of these values versus $1/T$ give straight lines only for temperatures less than 263 K. The spin-rotation occurs for $T > 263$ K and can be evaluated from the differences of the observed relaxation rates at $T > 263$ K and of the extrapolated straight line from the low temperature region. The spin-rotation relaxation times are shown on Table 6. The spin-rotation coupling constant is $(\overline{C_0}^2)^{1/2} = 5 \pm 1$ khz, much less than for fluorine in the acetone, but much higher than for proton in methanol (negligible).

The intramolecular dipole-dipole fluorine times are calculated from formula (11) in the same manner as previously. The values are shown on Table 6. The differences between the measured fluorine relaxation rates minus the spin-rotation contribution at high temperatures and the calcu-lated ones are shown on Table 6 and are the intermolecular fluorine re-laxation rates. These values have to be compared with the values obtained from aromatic and benzylic protons (the ratio has to be $(\gamma_F/\gamma_H)^2$. The observed ratio is $T_{1r-HD}^{o}/T_{1r-FD}^{o} \sim 0.7$. The intermolecular interaction seems to be higher when measured from fluorine than from proton. The activation energy is 11 kJ mol^{-1} a rough value taking account of the extrapo-lation and differences between calculated and measured relaxation times. The corresponding values for protons are : 7 for aromatic and 9 for benzy-lic protons. The measured value seems to be closer for fluorine than for protons to the activation energy of the viscosity.

The calculated and experimental NOE measurements extrapolated to infi-nite dilution are in good agreement,measured : $f_F^o(H) = 0.28$, calculated $f_F^o(H) = R_{1a}^o/R_1^o = 0.30$ at 303 K. As $R_{1a}^o = R_1^o - R_{1r-FD}^{DDo_F}$, it means that the NOE measurement indicates the existence of the intermolecular inter-actions.

CONCLUSION

All these measurements and treatments confirm the information from paper III in solvation in the two solvents and the validity of the separation of the different contributions of proton and fluorine rela-xation rates from paper II and III.

The linearity of the plot of the measured relaxation rate versus the molar fraction of the solute, the relatively high value of the fluorine spin-rotation coupling constant, and the absence of intermolecular dipole-dipole interaction in acetone suggest poorly solvated molecules (in cohe-rence with the small values of energy barrier). The curvature of the plot

of the measured relaxation rate versus the molar fraction of the solute, the relatively low value of the fluorine spin-rotation coupling constant and the importance of intermolecular dipole-dipole interaction with a relatively high activation energy suggest a well solvated molecule (in agreement with the high value of energy barrier) in methanol.

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