HIGH-PRESSURE HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE: PRESSURE DEPENDENCE OF THE HINDERED ROTATION OF THE AMIDE-GROUP IN HIGHER AMIDES

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The study of the temperature dependence of the exchange broadened NMR-spectra has become the most prominent method for the determination of the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, intra- and intermolecular rearrangements.

Recently two groups (1,2) developed high-pressure high-resolution NMR cells capable of obtaining spectra in wide temperature range at pressures up to 300 MPa with a resolution $\leq$ 1 Hz, and applied these cells for the determination of the activation volumes $\Delta V^{\ddagger}$ of inorganic reactions (2) and organic intramolecular rearrangements (3).

The first class of compounds studied extensively in our group, were the N,N-dimethylamides. The activation volume for the inversion of the dimethylaminogroup ($R_1 = CH_3$) in most solvents is around +10 $cm^3 \cdot mol^{-1}$ (3).

Two different explanations have been given for this magnitude and the positive sign of $\Delta V^{\ddagger}$. Le Noble (4) proposed, that the reduction of the dipole-dipole-attraction in the transition state is responsible for the volume increase found. Our group proposed that the effect is best described by a simple sterical model (3). In order to rotate around the N-C(=O)-bond, the dimethylaminogroup requires that a toroidal volume must be kept free of other molecules. The dislodgement of the solvent molecules during this rotation is the main cause for the volume effects observed.

The study of the pressure dependence of unsubstituted amides (R_1=H) where the electrostriction effects are maximal and geometrical effects minimal, and the study of symmetrical N-alkylamides with ethyl- (R_1=C_2H_5-) or isopropylgroups (R_1=1 iC_3H_7), where electrostriction effects are reduced and sterical effects enhanced, should reveal which of the mechanisms is responsible for the effects observed.

We have therefore studied the pressure and temperature dependence of the proton high resolution NMR spectra of N,N-diisopropylbenzamide (DiPrB), N,N-diethylbenzamide (DEB), acetamide (AA) and formamide (FoA). Computer simulation of the complex exchange broadened A_6B, A_3B_2 and ABC_n spectra, by application of the DNMR 5 program, yields the inversion rate for the rotation of the amide group as function of pressure and temperature. In fig. 1 typical spectra for DiPrB at 150 MPa are given. Table 1 compares the activation volumes derived from the analysis of the spectra of all amides with some results obtained previously for two dimethylamides. The results available to date corroborate qualitatively the geometrical model proposed for the dimethylamides: DEB and DiPrB do show relatively large activation volumes while the effects found in AA and FoA are much smaller. However, the results do reveal also the quantitative limitations of the simple sterical model proposed (3). The activation volume of the primary amides can still be described with sufficient accuracy by this model. The substitution of the amide protons by two ethyl- resp. isopropylgroups introduces two conformationally flexible groups into the rotating moiety. The preferred torsion angles of these groups around the N-C bond are unknown, and it is thus impossible to extend the model calculations to these groups. Theoretically one would expect at least a slight

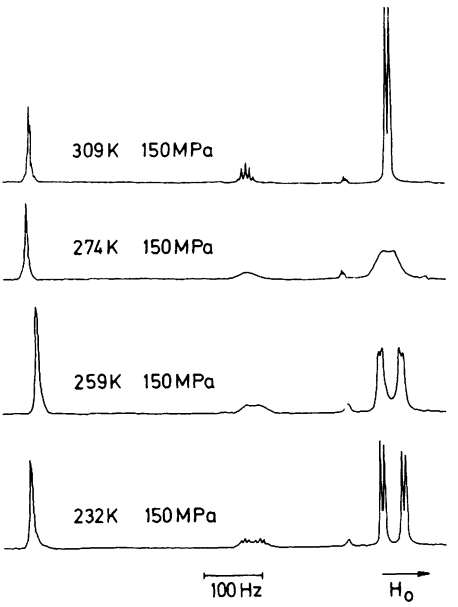

Fig. 1: T-dependence of the DiPrB proton spectra at 150 MPa

increase of $\Delta V^{\ddagger}$ when the dimethylaminogroup is replaced by a diethylaminogroup. Experimentally a slight decrease is observed when DMB and DEB are compared.

TABLE 1

$\Delta G^{\ddagger}$ and $\Delta V^{\ddagger}$ of the Amide Inversion in Symmetrical Amides

R_1	R_2	Solvent	Conc. (%w/w)	$\Delta G^{\ddagger}$ (5MPa) $kJ \cdot mol^{-1}$	Lit.	$\Delta V^{\ddagger}$ $cm^3 \cdot mol^{-1}$
CH_3	CH_3	Acetone	20	75	75	10.0
C_6H_5	CH_3	- " -	"	62.5	62	8.6
-"-	C_2H_5	- " -	"	61	-	7.4
-"-	$CH(CH_3)_2$	- " -	"	57	-	5.4
CH_3	H	Acetone/DMF (1:1)	"	71	70	2.2
H	H	Acetone	10	69	74.5	2.3

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