Ring Inversion in 1,3-Dioxane and 1,3,5-Trioxane as Studied by Proton Magnetic Resonance

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The ring inversion of several cyclohexane-like molecules has in recent years been studied with high resolution proton magnetic resonance techniques.[1] With the intention of studying the effect on the ring inversion of the substitution of methylene groups with oxygen atoms in the cyclohexane ring, we have studied the temperature dependence of the NMR-spectra of tetra-hydropyran, 1,3-dioxane, 1,4-dioxane and 1,3,5-trioxane. We will in this note give the results of the analysis of the temperature dependence of the spectra of 1,3-dioxane and 1,3,5-trioxane.

Acetone was used as solvent for 1,3-dioxane. No changes in the NMR-spectra with temperature could, however, be detected when acetone was used as a solvent for trioxane. With the use of *m*-fluorotoluene as solvent, however, the single line NMR-spectrum of trioxane observed at room temperature broadened into an AB quartet at lower temperature. No change in the single, sharp line from 1,4-dioxane could be detected down to −140°C in isoprene. The spectra of tetra-hydropyran were temperature dependent, but due to the complex shape of the spectra they could not be analyzed in detail.

The spectra were recorded on a Dual Purpose NMR spectrometer from Varian Asc. operating at 60 MHz. The sample was kept in a cryostat as described by Pople, Schneider and Bernstein.[2] The only difference from their more complicated experimental set up was a small teflon plug with helical groves inserted just above the sample tube in the cooling nitrogen inlet. The teflon plug apparently imparted a rotating motion of sufficient strength to the incoming nitrogen to spin the sample tube.

We have based our analysis on the AB quartet observed from the protons in the $O-CH_2-O$ groups in both compounds. We have derived the mean lifetime of the molecules in one conformation, τ, from measuring the peak to valley ratio,[3] r, in the AB quartet. The relation between r and τ was calculated by using the theoretical expression derived by Alexander [4] for two mutually coupled protons exchanging sites. From this expression a series of theoretical spectra was calculated for different values of τ based on the experimentally observed low temperature chemical shifts

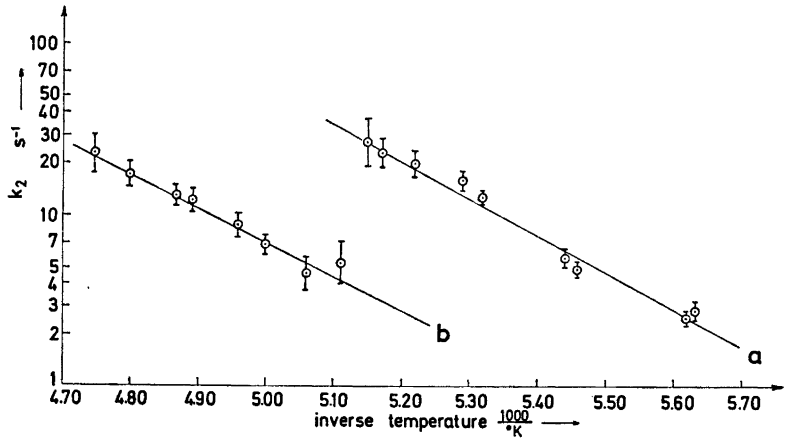

Fig. 1. The observed rate constant of the chair-chair inversion process k_2 in a) 1,3-dioxane and b) 1,3,5-trioxane as a function of temperature.

Table 1. The derived thermodynamical quantities and the observed chemical shifts and coupling constants at low temperature for 1,3-dioxane and 1,3,5-trioxane.

Compound	δ (Hz)	J (Hz)	$\Delta G_{cc}^{\ddagger}$ (kcal/mole)	$\Delta H_{cc}^{\ddagger}$ (kcal/mole)	$\Delta S_{cc}^{\ddagger}$ (cal/mole degree)	Coalescence temperature (°K)
1,3-Dioxane	18.2	6.5	9.9 ± 0.2	9.5 ± 0.5	-2 ± 3	194.0 ± 2.0
1,3,5-Trioxane	20.5	6.5	10.9 ± 0.2	8.8 ± 1.2	-10 ± 6	210.5 ± 2.0

and coupling constants. From these spectra r was computed and a curve constructed giving the relation between r and τ. This curve was then used to convert the observed r-values to τ-values. In Fig. 1 the observed values of k_2 are given. k_2, the rate constant for the chair-chair inversion process, is equal to $1/\tau$. Using the theory of absolute reaction rates the values of the standard Gibb's activation energy, $\Delta G_{cc}^{\ddagger}$, the activation enthalpy, $\Delta H_{cc}^{\ddagger}$ and the activation entropy, $\Delta S_{cc}^{\ddagger}$ can be calculated for the chair-chair process from the following formulas:[5]

$$\Delta G_{cc}^{\ddagger} = 2.303 \cdot RT \left(\log \frac{k}{h} + \log T - \log k_2\right)$$

$$\Delta H_{cc}^{\ddagger} = 2.303 \cdot R \left(\frac{\delta \log k_2}{\delta (1/T)}\right)_P$$

$$\Delta S_{cc}^{\ddagger} = \frac{\Delta H_{cc}^{\ddagger} - \Delta G_{cc}^{\ddagger}}{T}$$

The obtained results are given in Table 1.

It is generally assumed that the inversion of cyclohexane from one chair conformation to the other goes through the boat conformation as an intermediate. The thermodynamic parameters can also be calculated for chair to boat instead of from chair to chair as:

$$\Delta S_{cb}^{\ddagger} = \Delta S_{cc}^{\ddagger} + R \ln 2 = \Delta S_{cc}^{\ddagger} + 0.9 \text{ cal/mole degree}$$

$$\Delta G_{cb}^{\ddagger} = \Delta G_{cc}^{\ddagger} - RT \ln 2 = \Delta G_{cc}^{\ddagger} - 0.3 \text{ kcal/mole (at 200°K)}$$

$$\Delta H_{cb}^{\ddagger} = \Delta H_{cc}^{\ddagger}$$

Our results given in Table 1 on 1,3-dioxane are in good agreement with the results in an earlier study by Anderson and Brand.[6]

Cyclohexane has been studied several times with proton magnetic resonance methods.[1] There seems to be general agreement that $\Delta G_{cc}^{\ddagger} = 10.0$ kcal/mole and $\Delta H_{cc}^{\ddagger}$ has a value between 9.1 ± 0.1 kcal/mole [7] and 10.8 kcal/mole.[8] The value of $\Delta S_{cb}^{\ddagger}$ is quite uncertain, however, Allerhand, Chen and Gutowsky [7] find $\Delta S_{cb}^{\ddagger} = -5.8 \pm 0.4$ cal/mole degree and Anet and Bourn [8] find $\Delta S_{cb}^{\ddagger} = 2.8$ cal/mole degree.

Comparing these values of the activation parameters of cyclohexane with our values given in Table 1, it is surprising to see that the introduction of two or three oxygen atoms into the cyclohexane ring seems to have only a minor effect on $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$. These results, therefore, indicate that the lone pairs on the oxygen atoms play the same part as the hydrogen atoms in the methylene groups in the stabilization of the chair conformation.

Our values of the activation entropy are so uncertain that they do not permit any conclusions regarding the symmetry of the activated complex to be drawn.

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