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^{1}H-DNMR STUDIES ON THE CIS-TRANS ISOMERISM OF DIAZOACETYLCHLORIDE AND ITS DERIVATIVES

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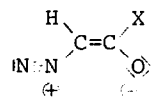
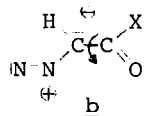
Abstract : Diazoacetylchloride and its ester derivates show a kinetically caused NMR-line shape for the CH-proton, due to a cis-trans isomerism.

As could be shown recently, the formerly unknown diazoacetylchloride[1] can be synthesized from phosgene and diazomethane. In the NMR-spectra a temperature dependent line shape[2] can be observed for the CH-proton, which is due to the kinetics of a cis-trans rearrangement, known for α-diazoketones[3,4,5]. At temperatures below 0°C, sharp and separate signals are obtained for both isomers (A : high field signal δ_A=5.2 ppm, B : low field signal δ_B=5.5 ppm). The kinetic data are presented in the following table. Also included are two ester derivatives, resulting from the reaction of diazoacetylchloride with C_6H_5OH and $O_2N(C_6H_4)OH$, respectively[1].

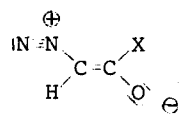
1 : $N_2CHCOCl$ 2 : $N_2CHCOOC_6H_5$ 3 : $N_2CHCOOC_6H_4NO_2$



a



b



c

A (low field signal) $\underset{k_B}{\overset{k_A}{\rightleftharpoons}}$ B (high field signal)

Rate constants and activation parameters for the cis-trans isomerization of diazoacetylchloride and its derivatives[a].

	k_A(25°C) s^{-1}	k_B(25°C) s^{-1}	$\Delta H_A^{\ddagger}$ kJ/mol	$\Delta H_B^{\ddagger}$ kJ/mol	$\Delta S_A^{\ddagger}$ J/K mol	$\Delta S_B^{\ddagger}$ J/K mol
1 (CCl_4)	16.6+1	19.5+1.2	47+2.5	49+2.5	-66+8	-56+8
2 (CCl_4)	(6.3+0.6)10^2	(9+0.9)10^2	51+3	52+3	-20+9	-16+9
3 ($CDCl_3$)	(2.8+0.3)10^2	(3.5+0.4)10^2	56+3	55+3	-13+9	-12+9

a) data obtained by line shape analysis, considering temperature dependence of K and .

The solvents employed were CCl_4 for 1 respectively 2 and $CDCl_3$ for 3. The results show, that at room temperature the slowest isomerisation rate is observed for diazoacetylchloride. Looking at the activation parameters, compound 1 has the smallest activation enthalpy and the most negative activation entropy. At room temperature however, the entropy effect is much more important and therefore a very low rate results for 1 in comparison to 2 and 3. Astonishingly small is the change in the activation enthalpy if the electron donor respectively electron acceptor properties of the substituents X are varied under the condition of similar steric properties of X in 2 and 3. This can be explained by the resonance forms a,b and c. An electron withdrawing group favours both, the resonance structures with a C-C double bond (a and c) and that with a single bond (b). Therefore effects occur, which compensate each other and lead to activation enthalpies being nearly independent of the nature of X. A similar behaviour seems to be valid, comparing the rotations around the C-N bond in $(CH_3)_2N\text{-}CO(CH_3)$ and $(CH_3)_2N\text{-}CO(CF_3)$[6]. Only small changes in the activation enthalpy (2 kJ/mol) are observed on the substitution of the CH_3 group by CF_3.

In parallel with the large change for the activation entropy, a different behaviour for the $C\underline{H}$ ^1H chemical shift is observed, in going from 1 to 2 respectively 3. In contrast to 2 and 3, for compound 1, the chemical shift difference between the cis and trans isomer is strongly temperature dependent. The same result is obtained for the equilibrium constant $K=k_A/k_B$, which can be given precisely by direct spectra integration. At 25°C, 1, 2 and 3 yield nearly the same value for K (0.77 ± 0.5), but only 1 gives a reaction enthalpy, significantly different from zero, resulting in a temperature dependent equilibrium constant. This can be explained by a strong solvation of molecule 1. From the negative activation entropy for the isomerisation process, it can be concluded that molecule 1 is more strongly solvated in the transition state than in the ground state. For the transition state, it can be assumed, that the resonance form b prevails, because of its free rotation around the C-C bond. Therefore a resonance structure such as b is favoured by CCl_4 solvation in comparison to the structures a and c.

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