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Calorimetric and spectroscopic investigations into the stability of $SiCl_4$ and $SnCl_4$ complexes.

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Abstract

The enthalpy values for the reaction of acetoacetanilides with $SiCl_4$ and $SnCl_4$ have been determined by solution calorimetry at 298 K in 1.2-dichloroethane. Stable compounds were isolated and identified by elementary analysis and spectroscopic methods.

Introduction

As shown in our previous investigations there is a connexion between the formation enthalpy of Lewis acid - Lewis base complexes and the substituents at the phenylring of the acetoacetanilides (1,2). Basing on these experiments we used $SiCl_4$ and $SnCl_4$ as Lewis acids.

Experimental

1. Calorimetric measurements

The calorimetric measurements were carried out with the 8700 LKB system at 298 K in 1.2-dichloroethane as solvent. We used tris(hydroxymethylaminomethane)as a standard for calibration of the equipment.

2. IR-spectra

The infrared spectra were recorded in the range of 200-400 cm^{-1} as KBr pellets respectively as nujol suspensions using the Perkin-Elmer IR-spectrograph 225.

3. ^{1}H-NMR-spectra

The proton resonance spectra were registered with the Perkin-Elmer 60 mHz apparatus of the type R 12. We used DMSO-d_6 as a solvent and TMS as an internal standard.

4. Elementary analyses

The elementary analyses were done by Beller Laboratories in Göttingen.

Results

By Lewis acid - Lewis base reactions between $SiCl_4$, $SnCl_4$ and various substituted acetoacetanilides (see Fig.1) we determined the formation enthalpy of metal complexes depending on the kind and position of the substituents R_1 and R_2.

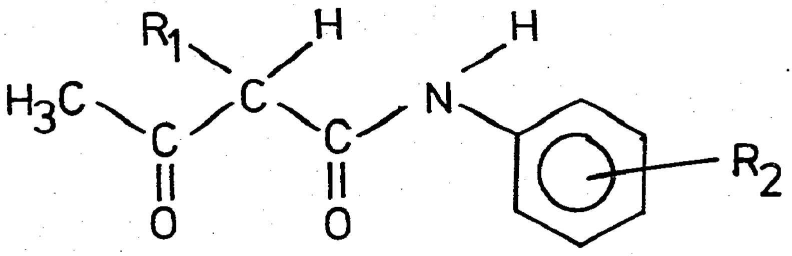

Figure 1 substituted acetoacetanilide R_1= H,Cl,CH_3, R_2=H,p,m,o,-CH_3
p,m,o,-OCH_3
p,-F,Cl,Br,J

Table 1 shows the formation enthalpy values of the $SiCl_4$ complexes. The $SnCl_4$ data were reported in an earlier paper(1)

Table 1

Formation enthalpies of the $SiCl_4$-complexes

Acetoacet-	$-\Delta H_f$ kJ/mol^{-1}		$-\Delta H_f$ kJ/mol^{-1}
anilide	54,508	p-chloroacetoacetanilide	52,007
p-anisidide	55,973	m-chloroacetoacetanilide	49,483
m-anisidide	63,172	o-chloroacetoacetanilide	45,978
o-anisidide	55,424	p-fluoroacetoacetanilide	57,030
p-toluidide	56.572	p-bromoacetoacetanilide	48,356
m-toluidide	55,982	p-iodoacetoacetanilide	46,826
o-toluidide	56,130		

The enthalpy values (see table 1) of the metal complexes were influenced by the substituents at the phenylring of the acetoacetanilides. The electron density at the amid nitrogen atom is of great importance regarding the stability of the metal complexes and can be described by the Hammett equation. The negative rise of the graph indicates that the increasing electron density at the reaction center, the amid nitrogen, is favourable to the course of reaction. The plot of the enthalpy differences of in para position halogenated $SiCl_4$ complexes against the substituent constants gives decreasing stability of the metal complexes with decreasing positive mesomeric effect of the halogen atoms following the order

$$F > Cl > Br > I$$

The same graduation of the substituent effect results from the correlation between the ΔH_f-values of the $SiCl_4$ compounds with the pK_b-values of the corresponding anilines (see Fig.2).

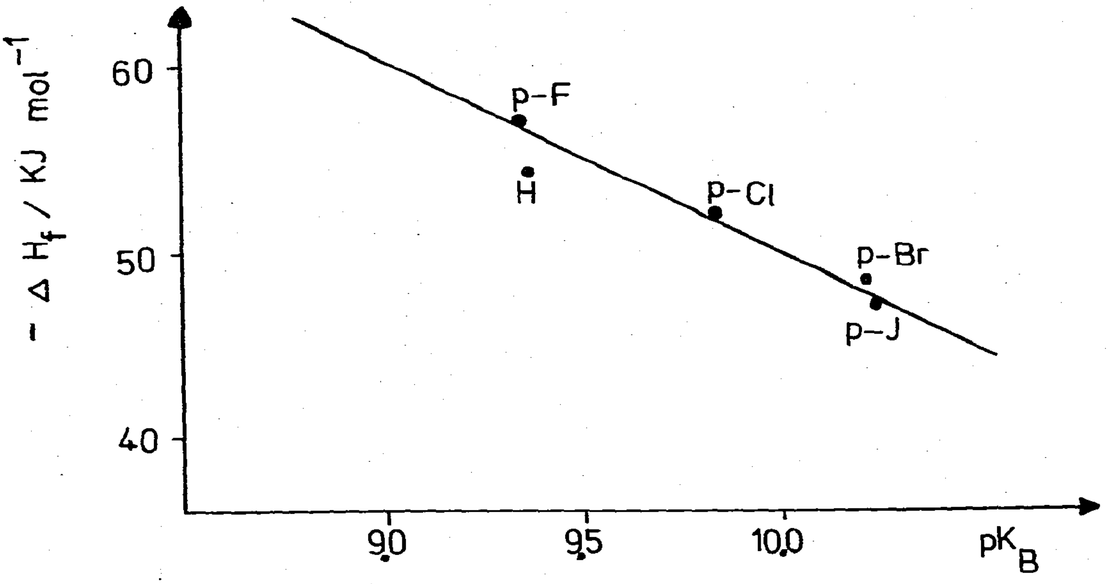

Figure 2 Plot of the formation enthalpy values of the $SiCl_4$complexes against the pK_b values

The effect of substituents in α-position of the acetoacetanilides on the stability of metal complexes has been described several times (3,4,5). These investigations have proved that the influence of substituents directly combined with a carbon atom of the metal containing area is much greater regarding complex stability as substituents at the phenylring. Figure 3 shows by example of the $SnCl_4$ compounds the decreasing stability caused by a substituted chlorine atom in α-position of the chelate ring.

The infrared ^1H-NMR data and the results given by elementary analysis indicate in the case of the $SnCl_4$ complexes a 1:1 adduct structure. The Lewis acid is coordinated with the acetoacetanilide by the carbonyl oxygen adjacent to the nitrogen atom ($SnCl_4$ acetoacetanilide). We assign to the $SiCl_4$ complexes the composition 1:3 chelates of the type $SiCl_4(acetoacetanilide)_3HCl_2$. This is in accordance with structural proposals of several authors who used acetylacetone as complexing agent (6,7,8)

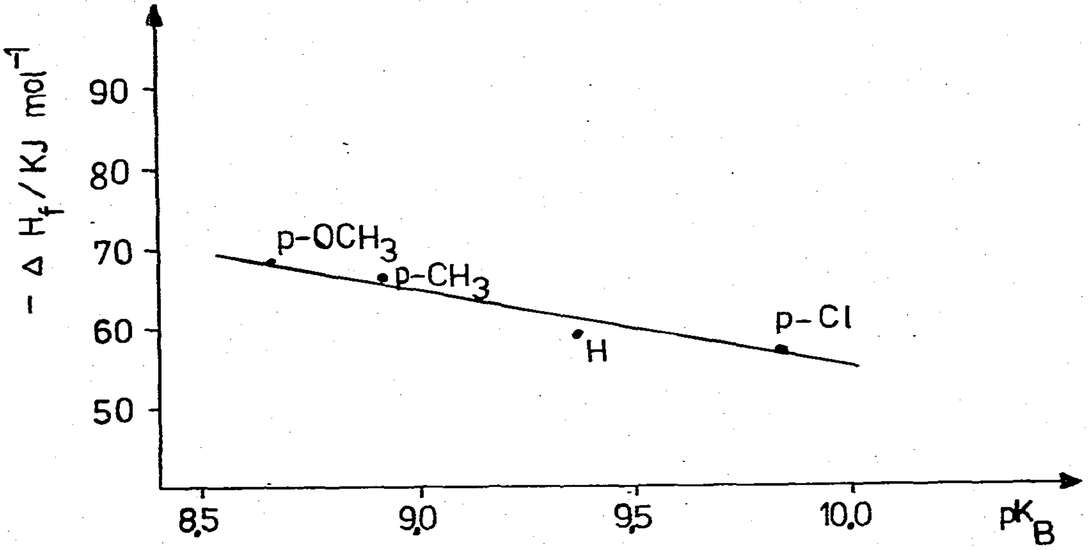

Figure 3 Plot of the formation entalpy values of the $SnCl_4$ complexes against the pK_b values

Acknowledgement

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