

Calorimetric Studies of Adduct Formation between Antimony Pentachloride and Methanol, Methyl Propyl Ether and Dipropyl Ether

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In a previous communication, a value for the enthalpy of adduct formation between antimony pentachloride and water in ethylene chloride solution has been reported.¹ In order to obtain information of the influence on the enthalpies of adduct formation of substituting alkyl groups for hydrogen atoms in water calorimetric experiments have been performed using methanol, methyl propyl ether and dipropyl ether as donors.

*Experimental.** Materials.* Ethylene chloride was treated as given in Ref. 1 and antimony pentachloride as given in Ref. 3.

Dipropyl ether (Fluka) was fractionally distilled after drying with Drierite. *Methyl propyl ether* was synthesized from propyl bromide and sodium methylate (*cf.* Ref. 4). The azeotropic mixture of ether and methanol obtained by distillation from the reaction mixture was dissolved in ligroin and the solution washed with water. The ether was separated from the ligroin by fractional distillation after drying the solution with Drierite. The purity of the ether samples was checked by analytical GLC using dinonyl phthalate as stationary phase on Chromosorb P and in addition polyethylene-glycol 1000 on Celite for methyl propyl ether and Carbowax 1500 on Chromosorb G for dipropyl ether. The purity was judged to be better than 99.9 %.

Methyl propyl ether	n_D^{25}	1.3543	d_4^{25}	0.7203
Dipropyl ether	n_D^{25}	1.3780	d_4^{25}	0.7422

A pure sample of *methanol* was supplied by Dr. I. Wadsö at this laboratory (*cf.* Ref. 5). The water content of the donor samples was

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** *Apparatus, Calibration, Calorimetric Procedure and Correction to standard states*, see Ref. 2.

checked by gas chromatography using a Porapak Q column,^{6,7} and was found to be less than 0.01 % by volume for all three samples.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie equal to 4.1840 abs. joules and refer to the isothermal process at 25°C and to the true mass.

Results. The experimental results are summarized in Table 1. Column 1 shows

Table 1. Enthalpy changes accompanying the formation of adducts between $SbCl_5$ and different donors in ethylene chloride solution.

Donor	$-\Delta H_1$ kcal-mole ⁻¹	$-\Delta H_2$ kcal-mole ⁻¹	$-\Delta H$ kcal-mole ⁻¹
H_2O^a	—	—	24.3 ± 0.3
CH_3OH	16.09	-2.99	19.08 ± 0.02
$C_3H_7OCH_3$	18.07	-0.02	18.09 ± 0.02
$(C_3H_7)_2O$	17.23	-0.61	17.84 ± 0.02

^a Ref. 1.

the means of five determinations of the heat evolved in the reaction of liquid donor with antimony pentachloride in ethylene chloride solution. The results from the measurements of enthalpies of solution of donors in pure ethylene chloride are shown in column 2. Three experiments were performed on each ether and four on methanol. In the concentration region used (0.01–0.04 M) it can be assumed that the content of methanol polymers in solution is negligible, *cf.* Ref. 8. The calculated values for the enthalpy change for the reaction with both reactants and reaction product in ethylene chloride solution are given in column 3. The error limits are expressed as standard deviation of the mean.

The previously reported $-\Delta H$ value for water has been included in Table 1.

An enthalpy value of -17.9 ± 0.5 kcal-mole⁻¹ has been reported for ethanol⁹ but may not compare with the values given in Table 1 as it is uncertain to what state of ethanol it refers.

Discussion. In the series of donor molecules water-alcohol-ether, hydrogen atoms are replaced by alkyl groups and the substitutions are accompanied by increased dimensions of the molecules and a decrease in their ionization energies, *e.g.* H_2O 12.6

eV, CH_3OH 10.8 eV, and $(\text{CH}_3)_2\text{O}$ 10.0 eV.¹⁰ In contrast to what could be expected from the trend in the ionization energies the $-\Delta H$ values for adduct formation with SbCl_5 as acceptor have been found to decrease in following way: water > methanol > methyl propyl ether. The same order in donor strength between alcohols and ethers has been found with BF_3 as acceptor and using ΔG as a measure of the strength of interaction.¹¹ In these acceptor molecules the halogen atoms may interact with the groups attached to the donor atom and give rise to steric strains in the adducts and possibly to some extent reduce the donor strength of ethers. It has namely been found that ethers give higher $-\Delta H$ values than alcohols for complex formation with the much weaker acceptor I_2 ,¹² where steric interactions between donor and acceptor molecules could be expected to be less influential. The data are not, however, conclusive as the influence of the self-association of alcohols seems not to have been taken into account.

It was concluded from qualitative experiments on enthalpies of adduct formation that ethers and ketones showed comparable donor strengths towards SbCl_5 and SnCl_4 as acceptors.¹³ This is confirmed by the results found in this investigation. The $-\Delta H$ values for the ether adducts are, however, slightly higher than for ketone adducts,¹⁴ but the differences are too small to permit any valid conclusions.

Considering the $-\Delta H$ values found for methyl propyl ether and dipropyl ether (18.1 and 17.8 kcal-mole⁻¹, respectively) the value for diethyl ether can be expected to be close to 18.0 kcal-mole⁻¹. A recently reported value¹⁵ of 19.2 kcal-mole⁻¹ thus seems to be about 1 kcal-mole⁻¹ too high.

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A Simple One-pot Procedure for the Synthesis of Certain Substituted Thiophene Aldehydes and Ketones

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Starting from the dibromothiophenes, various disubstituted thiophenes are available through step-wise halogen-metal interconversion followed by reaction of the bromothiennyllithium derivative with an appropriate reagent, provided that the group introduced first does not interfere with the second halogen-metal exchange (for review, *cf.* Ref. 1).

Substituted thiophene aldehydes were prepared by reacting the bromothiennyllithium derivative with *N,N*-dimethylformamide, protecting the formyl group of the bromothiophene aldehyde formed through acetal formation, followed by a second halogen-metal exchange and reaction with an appropriate reagent. This method was first introduced by Goldfarb *et al.*,² who found that the acetals of thiophene aldehydes as well as of thienyl ketones were