

Enthalpy of Adduct Formation between Antimony Pentachloride and Water

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The enthalpy of adduct formation between antimony pentachloride and water has been determined calorimetrically. The value obtained was $-24.3 \text{ kcal.mole}^{-1}$ and this refers to adduct formation where both reactants and reaction product are in ethylene chloride solution.

It is impossible, without an elaborate technique, to completely remove water from ethylene chloride. In the standard calorimetric procedure to determine enthalpies of adduct formation, excess antimony pentachloride was added prior to the experiment to remove traces of water.¹ The uncertainty in the amount of free acceptor did not impair the accuracy of the determinations. From calorimetric experiments on adduct-formation reactions, it was possible to determine enthalpies and stability constants simultaneously, but it was necessary to know the concentration of the free acceptor.² This was found by subtracting the amount of SbCl_5 reacting with the total amount of water present in an experiment from the known amount of acceptor added. Therefore, in separate calorimetric runs, an ampoule containing SbCl_5 was broken in ethylene chloride under the precise conditions of the experiments. The heat evolved, corrected for the heat of solution of SbCl_5 , will give the amount of reaction directly, provided the value for the heat of formation of the $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct is known (reactants and product in ethylene chloride solution).

The reaction between antimony pentachloride and water has been investigated by Anschütz and Evans.³ A crystalline product of composition $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ was obtained when equimolar amounts of the reagents were mixed in chloroform. With excess water, crystals of composition $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$ were obtained. From the monohydrate, antimony pentachloride could be recovered by distillation under reduced pressure.

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EXPERIMENTAL *

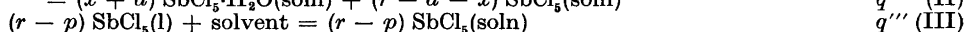
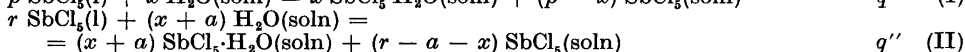
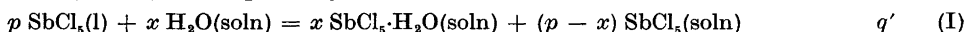
Materials. Ethylene chloride (Fisher Certified Reagent) was distilled (cf. Ref. 1) immediately before use. Purity was checked by GLC with dioctylphthalate on Chromosorb P as stationary phase. No impurity was found. Antimony pentachloride was treated as given in Ref. 4. It was transferred by suction, in an atmosphere of dry nitrogen into 1 ml ampoules furnished with two capillary shafts, which were then sealed off. Ethyl propionate was fractionally distilled after drying with Drierite. Purity was checked by analytical GLC using polyethyleneglycol on Chromosorb P as stationary phase and by titration after alkaline hydrolysis which indicated 99.9 % purity.

Calorimetric Procedure. Two different 1 l quantities of ethylene chloride labelled R and S, containing unknown amounts of water, were each divided into two half-portions. One portion of each was used for blank determinations. To the other samples were added 37.6 and 69.3 μg of water per g of ethylene chloride, these samples were marked R_w and S_w, respectively. The calorimeter was charged with 126.0 g of one of these samples of ethylene chloride. After equilibration the reaction was started by breaking the glass ampoule containing an excess of antimony pentachloride.

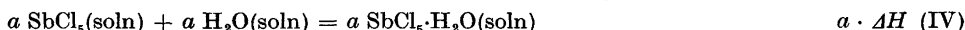
In another set of experiments ethylene chloride solutions containing varying amounts of water were used. After having performed an experiment, using an excess of SbCl₅, a second ampoule containing an excess of ethyl propionate was introduced into the system. The amount of SbCl₅·ethyl propionate adduct formed was determined from the heat evolved and the knowledge of the enthalpy of formation of this adduct.⁵ The difference between the amount of SbCl₅ added to the system and ethyl propionate adduct formed was taken as the amount of SbCl₅·water adduct formed in the first reaction.

All reactions took place instantaneously and the reaction periods were less than 5 min. The heat leakage constant values (*K*) for the experiments in which the final reaction solutions contained free SbCl₅ deviated, however, from *K*-values obtained in the calibration experiments and in experiments where ethyl propionate was in excess. A slow heat evolution in the final periods of the reaction experiments was the reason for this difference, which was independent of the amount of water adduct present in the reaction mixture. The most probable explanation is that SbCl₅ slowly reacted with water from the vapor space above the calorimetric liquid. This secondary effect, however, did not influence the true determination of the heat evolved in the experiments as the initial and final resistance values were obtained graphically (cf. Ref. 6).

Corrections to standard states. The enthalpy change accompanying the isothermal reaction (IV) with reactants and reaction product in ethylene chloride solution was obtained from heat of reaction and heat of solution experiments corresponding to reactions (I) – (III), respectively.



Subtracting eqns. (I) and (III) from (II) gives the hypothetical reaction



Here, *x* is the unknown and *a* the known added amount (in mmoles) of water present in 126.0 g of ethylene chloride. *p* and *r* are the amounts of SbCl₅ (mmoles) added in the experiments; *p*, *r* > *a* + *x*. ΔH is the enthalpy of formation of SbCl₅·H₂O (in cal/mole equal to kcal/mole). *q'*, *q''*, and *q'''* are the amounts of heat (in cal) evolved.

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.

* *Apparatus and Calibrations*, see Ref. 1.

RESULTS AND DISCUSSION

The experimental results are summarized in Tables 1—3. The heat equivalent, ε° of the system used was 1116.4 ± 0.2 cal per unit of $2 \times 10^2 (R_i - R_f)/(R_i + R_f)$. In the heat of reaction measurements (Table 1) the first column

Table 1. Heat of reaction measurements performed in ethylene chloride solutions containing water.

Ethylene chloride sample	mmole SbCl_5	$2 \times 10^2 (R_i - R_f)/(R_i + R_f)$	q cal
R	0.952	0.414	4.24
	1.108	0.478	4.88
	1.417	0.485	4.83
			4.65 ± 0.22
Rw	0.912	0.916	9.84
	1.180	0.937	9.98
	1.556	1.055	11.12
			10.31 ± 0.44
S	1.153	0.507	5.19
	1.249	0.517	5.25
	1.974	0.549	5.30
	2.555	0.546	5.03
		5.19 ± 0.09	
Sw	1.956	1.584	16.84
	2.840	1.634	17.05
	3.502	1.679	17.27
			17.05 ± 0.15

Samples R give $-\Delta H = 21.4 \pm 1.8$ kcal·mole⁻¹.

Samples S give $-\Delta H = 24.3 \pm 0.3$ kcal·mole⁻¹.

gives the ethylene chloride sample used in each set of experiments. Column 2 gives the amount of SbCl_5 and column 3 the temperature rise expressed in units of $2 \times 10^2 (R_i - R_f)/(R_i + R_f)$. The last column gives the heat evolved corrected for heat of solution of SbCl_5 . The calculated values of the molar enthalpy change are given at the end of the table. A summary of the experiments where the amount of excess SbCl_5 was determined by adduct formation with ethyl propionate is given in Table 2. The first column gives the amount of SbCl_5 , the second the temperature rise, and the third the heat evolved corrected for the heat of solution of SbCl_5 . The fourth column gives the amount of ethyl propionate added to the reaction mixture. The calculated amount of $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct formed is given in the fifth column and the enthalpy of $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ formation in the last column. The $-\Delta H$ value for ethyl propionate has been taken as 16.82 kcal/mole.⁵ The difference between

Table 2. Heat of reaction measurements, performed in ethylene chloride solution containing water and the excess SbCl_5 determined by adduct formation with ethyl propionate.

mmole SbCl_5	2×10^3 $(R_i - R_f)/$ $(R_i + R_f)$	q cal	mmole ethyl propionate	mmole $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct	$-\Delta H$ kcal/mole
0.561	0.480	5.13	1.104	0.215	23.8
0.710	0.929	10.07	1.065	0.456	22.1
0.930	1.729	18.88	0.908	0.752	25.1
					23.7 ± 1.0

the enthalpy of formation values for the water and ethyl propionate adducts is about 7 kcal/mole; it is thus unlikely that any measurable amount of $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ water adduct will dissociate when the second donor is added. The heat of solution experiments are summarized in Table 3. The first column gives the

Table 3. Heat of solution measurements of SbCl_5 in SbCl_5 -ethylene chloride solution.

mmole SbCl_5	previously added SbCl_5 , mmole	q cal	$-\Delta H$ kcal/mole
2.504	2.08	1.06	0.42
2.699	4.22	1.18	0.44
2.932	1.02	1.24	0.42
3.621	3.53	1.54	0.43
			0.43 ± 0.01

amount of SbCl_5 in the ampoule and the second the amount of SbCl_5 added prior to the experiment. Column 3 gives the heat evolved and the last column the molar enthalpy change. By performing the heat of solution experiments in SbCl_5 -ethylene chloride solution the interference of water was eliminated. The weighted mean for the enthalpy of adduct formation between antimony pentachloride and water calculated from the three series of determinations is -24.3 ± 0.3 kcal·mole⁻¹. The error limits are expressed as the standard deviation of the mean.

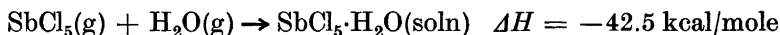
In the dilute solutions used the self-association of water is probably small (*cf.* Ref. 7). Reactions I, II and IV are written under the assumption that the water exists as solvated monomer in ethylene chloride.

The value for the molar enthalpy change calculated from the amount of water taking part in the reaction (Table 1) is the same as the value found when the extent of the adduct formation reaction is determined by antimony

pentachloride (Table 2). This shows that the composition of the complex is $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ at least as long as SbCl_5 is in excess and the solutions are dilute. It is most likely that a molecular addition compound is formed under these conditions. When an ampoule containing SbCl_5 was broken in ethylene chloride solution containing an excess of water (0.07 M) a white precipitate was obtained and a heat of reaction of -31.7 kcal per mole of SbCl_5 was found. This reaction was not further investigated.

Klages *et al.*⁸ have measured the temperature dependence of the decomposition pressure of $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ without, however, stating the nature of the decomposition products. From their results they calculated an enthalpy of "reaction" value of -17.8 kcal/mole. Webster⁹ has interpreted that value as being the enthalpy of formation of solid $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct from gaseous reactants.

It is easily seen that Webster's interpretation is not compatible with the present result. The heat of vaporization of water and SbCl_5 are 10.5 and 11.8 (estimated) kcal·mole⁻¹, respectively. The corresponding heat of solution values in ethylene chloride are -0.4 kcal/mole for SbCl_5 and $+4.5$ kcal·mole⁻¹ for water, the latter value calculated from the temperature dependence of the solubility.¹⁰ Combining these values with the heat of formation value determined for the adduct in solution, the enthalpy change of the following reaction is found:



If Webster's interpretation were correct, the heat of solution of $\text{SbCl}_5 \cdot \text{H}_2\text{O}(\text{c})$ in ethylene chloride must amount to something like -25 kcal·mole⁻¹, a value which is exceedingly improbable. The conclusion is therefore that Klages *et al.* have determined a total pressure for one or several unknown decomposition reactions.

Added in proof: A $-\Delta H$ value of 18.0 kcal. mole⁻¹ has been reported for the formation of the $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct (Gutman, V. and Mayer, U. *Monatsh. Chem.* **98** (1967) 294). This value cannot, however, be compared with the value found in this investigation as it is not stated to which standard state their value refers.

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