

## Adducts between Antimony Pentachloride and Carbonyl Compounds. A Calorimetric Study

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Heats of formation of a number of electron donor-acceptor adducts have been determined with both reactants and reaction products in 1,2-dichloroethane solution. Antimony pentachloride served as the acceptor molecule while a number of C=O compounds were donors. The following values were obtained:  $-\Delta H = 17.03$  kcal.mole<sup>-1</sup> (acetone), 16.38 (methyl acetate), 17.08 (ethyl acetate), 17.53 (isopropyl acetate), 16.76 (ethyl butyrate), 15.17 (methyl carbonate) and 15.98 (ethyl carbonate). The relative strengths of the donors have been discussed.

In a series of qualitative studies the orders of relative donor strengths of different donors with SbCl<sub>5</sub>, SnCl<sub>4</sub>, or SbCl<sub>3</sub> as acceptor molecules have been investigated<sup>1-5</sup>. In many cases these orders have been quite conclusive but the finer details cannot be clarified without accurate quantitative measurements. Such studies have been started and this paper will report the first results.

The reaction, Acceptor(g) + Donor(g) = Adduct(g), can as a rule not be studied directly but the measurements have been made in a solvent which has been assumed to give only weak interaction with the components as well as with the adducts, namely ethylene chloride. The results obtained have verified the assumption, the interactions of the donors with the solvent being only of the order of 0.1-0.4 kcal.mole<sup>-1</sup>. The heats of reaction of SbCl<sub>5</sub>(sol.) + Donor(sol.) = Adduct(sol.) can thus be considered as rather good measures of the gas phase reaction enthalpies.

The following donors have been studied: acetone, methyl acetate, ethyl acetate, isopropyl acetate, ethyl butyrate, dimethyl carbonate and diethyl carbonate.

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## EXPERIMENTAL

*Materials.* All chemicals used were commercial products. The regular procedure of purification has been drying (where not otherwise stated, with Drierite) followed by one or several distillations at atmospheric pressure or in vacuum. Three different all-glass columns were used packed with Fenske glass-helices. Column A of 35 theoretical plates and length 140 cm was operated with the reflux ratio 1:20, 250–300 ml being collected every 24 h, column B, 15 theoretical plates, 60 cm in length, and column C of 30 cm in length.

For most substances, except for the carboxylic esters, the purity of the samples was roughly estimated from melting curves obtained with a simple thinlayer, constant temperature difference apparatus<sup>8</sup>, using a calibrated resistance thermometer, 20 × 3 mm. Due to a small hysteresis effect, the accuracy of the given m.p.'s is not stated to better than 0.1°C. The purity of the carboxylic esters was determined by titration after alkaline hydrolysis.

Pure grade *ethylene chloride* (Eastman) was dried with calcium chloride and Drierite and distilled once through column A. The fractions boiling between 83.4 and 83.6° at 760 mm were used as solvent.

Analytical grade *acetone* was dried and distilled through column A. B.p. 56.20° at 760 mm. M.p. of the sample –95.0°. Purity better than 99.5 %.

One liter of ordinary *methyl acetate* was refluxed for 5 h with 100 ml of pure acetic anhydride and then distilled through a Vigreux column. The middle fraction was distilled in column A. B.p. 56.4° at 760 mm. Purity 99.9 %.

Pure samples of *ethyl acetate* and *isopropyl acetate* were analyzed and found to be of 99.9 and 99.8 % purity, respectively\*.

Technical grade *ethyl butyrate* was distilled through column C. The middle fraction was treated with solid K<sub>2</sub>CO<sub>3</sub> and Drierite at 60° for 2 h and then redistilled. B.p. 120.6° (uncorr.). Determination of the saponification equivalent gave a purity of 100.2 %.

Pure grade samples of *dimethyl carbonate* and *diethyl carbonate* were dried and distilled through column A. Purities were better than 99.5 % as estimated from the melting curves.

*Dimethyl carbonate*, b.p. 90.4° at 760 mm, m.p. 5.0°.

*Diethyl carbonate*, b.p. 126.5° at 760 mm, m.p. –77.4°.

Analytical grade *antimony pentachloride* was distilled under reduced pressure in column C. The main fraction was collected in a 250 ml two-necked flask, the second neck being equipped with a break-off seal. The neck connected to the distillation column was sealed off and the flask was sealed in an upside down position at *g* to another 250 ml two-necked flask, *f*, connected to an all-glass vacuum-line (Fig. 1). This consisted of a liquid nitrogen

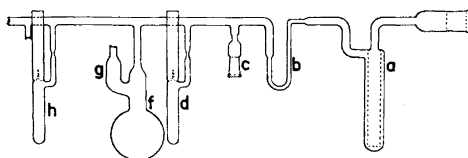


Fig. 1.

trap, *a*, a U-tube, *b*, which acted as a closed valve when containing frozen SbCl<sub>3</sub>, a standard joint, *c*, for attachment of a Pirani-gauge, a break-off ampoule, *d*, serving as receiver for a fore-run, and six 20 ml break-off ampoules, *h*, accommodating the main fraction.

The system was tested for leaks, evacuated to better than 10<sup>-4</sup> mm and thoroughly dried by flaming under continued pumping. The standard joint, *c*, was sealed off and the break-off seal in the flask containing ca. 150 ml SbCl<sub>3</sub> was opened by operating a solenoid acting on a glassenclosed iron-bar inside *g*. The liquid was rapidly emptied into *f*, when it was frozen to liquid nitrogen temperature and the original sample container was carefully sealed off at *g*.

\* Dr. I. Wadsö, Thermochemistry Laboratory, furnished the samples. His co-operation is appreciated.

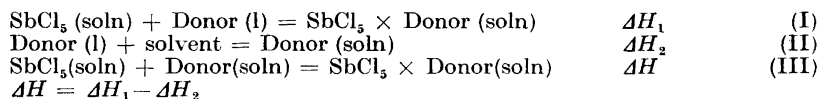
During the transfer of the sample, the U-tube, *b*, was wholly immersed in liquid nitrogen. Some  $\text{SbCl}_5$  was frozen out on the walls of the wider stem of the U-tube without blocking the vacuum-line. The system was now carefully evacuated and the sample was allowed to melt. A small amount of  $\text{SbCl}_5$  was distilled into the U-tube, and there frozen to give a solid plug, disconnecting the pumping system from the sample. Vapors of  $\text{SbCl}_5$  were allowed to reach all part of the glass line. The sample was again brought to liquid nitrogen temperature, the  $\text{SbCl}_5$  plug in the U-tube was melted and the substance distilled into the trap *a*. The system was carefully flamed and pumped out. The sample was again brought to room temperature and some of it was distilled into the U-tube and frozen to give a plug of solid  $\text{SbCl}_5$  extending into the wider part of the tube. About 10 ml of the sample was then distilled into the ampoule *d* which was sealed off and the bulk of  $\text{SbCl}_5$  was simultaneously distilled into the six ampoules *h*, which were then sealed off one by one. The ampoules were stored in the dark.

*Apparatus.* All experiments were carried out in a constant-temperature environment calorimeter (type D of Ref.<sup>7</sup>, a glass vessel had been substituted for the steel vessel), equipped with an electric heater, a thermistor and a central stirrer, accommodating a cylindrical one milliliter ampoule with thin end walls. The ampoule was broken by lowering the stirrer shaft so that a glass needle in the bottom of the calorimeter vessel broke through the end walls of the ampoule.

*Calibration.* The heat equivalent of the calorimeter including its content, was determined electrically by passing a known current for a given time (360 sec.) through the heating element. The calibration was performed on the system before the reaction had taken place. The result of each calibration experiment was adjusted to give the heat equivalent of a "standard system",  $e^\circ$ , in which the calorimetric liquid contained a certain amount of  $\text{SbCl}_5$  (1.00 g). For each experiment, the heat equivalent value used,  $e$ , was obtained from  $e^\circ$  by applying small corrections for the different amounts of donor compounds used, and for variations in the amount of  $\text{SbCl}_5$ .

*Calorimetric procedure.* The calorimeter was charged with 99.97 ml of ethylene chloride and 3–5 mmoles  $\text{SbCl}_5$ . After equilibration the reaction was started by breaking the sealed glass ampoule containing the donor compound. The reaction took place instantaneously and the reaction period was about 4 min. in all cases. The initial and final thermistor resistances ( $R_i$  and  $R_f$ , respectively) were obtained graphically.

*Corrections to standard states.* The enthalpy change accompanying the isothermal reaction III, with the reactants and the reaction product in solution, was obtained from the heat of reaction and solution experiments corresponding to eqns. I and II, respectively.



*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° and to the true mass. The molecular weights were computed from the 1957 table of atomic weights\*.

## RESULTS

The experimental results are summarized in Tables 1–3. Two slightly different systems were used, I and II, with heat equivalents  $3313 \pm 2$  and  $3326 \pm 2$  cal per unit of  $\log R_i/R_f$ , respectively. In Tables 1 and 2 the first column gives the name of the donor, the system used, within brackets, and the value of a correction,  $q$ , which should be added to the heat evolved to compensate for (a) heat effects caused by evaporation of solvent and condensation of donor due to incomplete filling of the ampoules, and (b) the heat of reaction between  $\text{SbCl}_5$  and the minute quantity of water adsorbed to the interior surface of the ampoules, as determined in blank experiments. It was assumed that all donor present as vapor inside the ampoule reacted with  $\text{SbCl}_5$ .

Table 1. Heat of reaction measurements performed in ethylene chloride solutions containing an excess of  $\text{SbCl}_5$  as acceptor.

Donor	mmole	g $\text{SbCl}_5$	$10^4 \cdot \log R_i/R_f$	$-\Delta H$ kcal/mole
Acetone (I) $q = -0.06$ cal	1.170	0.83	61.77	17.44
	1.859	1.45	97.60	17.41
	2.127	1.24	112.04	17.46
	2.510	1.26	131.46	17.37
	3.947	1.56	205.18	17.27
				17.39 $\pm$ 0.03
Methyl acetate (II) $q = -0.07$ cal	1.020	0.79	51.04	16.58
	1.201	0.77	60.57	16.61
	1.492	0.81	74.73	16.62
	3.758	1.53	186.95	16.60
				16.60 $\pm$ 0.01
Ethyl acetate (I) $q = -0.02$ cal	0.681	1.17	35.69	17.34
	0.937	1.23	49.21	17.40
	0.967	1.25	50.69	17.37
	2.890	1.44	150.45	17.29
	3.157	1.58	163.49	17.22
				17.32 $\pm$ 0.03
Isopropyl acetate (I) $q = -0.02$ cal	0.710	1.50	38.02	17.74
	1.275	1.61	67.72	17.63
	2.471	1.62	131.21	17.66
	2.546	1.58	136.15	17.79
	3.142	1.77	166.30	17.63
				17.69 $\pm$ 0.03
Ethyl butyrate (II) $q = 0.00$ cal	1.062	0.92	53.54	16.79
	1.134	1.00	57.30	16.83
	1.447	0.99	73.07	16.82
	3.112	1.26	158.15	16.97
				16.85 $\pm$ 0.04
Methyl carbonate (II) $q = -0.02$ cal	1.128	0.92	51.84	15.28
	1.288	1.06	59.50	15.36
	1.444	0.79	66.62	15.34
	3.092	1.20	141.66	15.28
				15.32 $\pm$ 0.04
Ethyl carbonate (I) $q = 0.00$ cal	0.614	1.41	30.28	16.36
	1.168	1.28	57.14	16.24
	2.071	1.40	101.57	16.29
	2.367	1.42	115.95	16.28
	3.202	1.51	157.60	16.38
				16.31 $\pm$ 0.03

and that its volume was replaced by the same volume of ethylene chloride vapor.

The second column gives the amount of donor added. The third column in Table 1 gives the total amount of  $\text{SbCl}_5$  added. The symbol  $\log R_i/R_f$  is

Table 2. Heat of solution measurements of the different donors in ethylene chloride.

Donor	mmole	$10^4 \cdot \log R_1/R_f$	$-\Delta H$ kcal/mole
Acetone (I) $q = -0.02$ cal	4.967	5.524	0.36
	4.442	4.995	0.37
	4.564	4.930	0.35
	4.282	4.580	0.35
	4.771	5.073	0.35
			$0.36 \pm 0.00$
Methyl acetate (II) $q = -0.03$ cal	4.018	2.706	0.22
	4.477	3.020	0.22
			$0.22 \pm 0.00$
Ethyl acetate (I) $q = 0.00$ cal	2.984	2.070	0.23
	3.528	2.473	0.24
	2.926	2.054	0.24
			$0.24 \pm 0.00$
Isopropyl acetate (I) $q = 0.00$ cal	2.662	1.197	0.15
	2.534	1.112	0.15
	2.930	1.478	0.17
	2.673	1.304	0.16
			$0.16 \pm 0.01$
Ethyl butyrate (II) $q = 0.01$ cal	3.666	0.837	0.08
	3.266	0.797	0.09
	2.564	0.668	0.09
			$0.09 \pm 0.00$
Methyl carbonate (II) $q = 0.00$ cal	3.489	1.636	0.16
	3.072	1.392	0.15
	4.920	2.269	0.15
	3.533	1.712	0.15
			$0.15 \pm 0.00$
Ethyl carbonate (I) $q = 0.02$ cal	2.568	2.555	0.34
	2.721	2.734	0.34
	2.588	2.491	0.33
	2.417	2.298	0.32
			$0.33 \pm 0.01$

Table 3. Enthalpy changes accompanying the formation of adducts between  $SbCl_5$  and different donors in ethylene chloride solutions.

Donor	$-\Delta H_1$ kcal.mole $^{-1}$	$-\Delta H_2$ kcal.mole $^{-1}$	$-\Delta H$ kcal.mole $^{-1}$
$Me_2CO$	17.39	0.36	$17.03 \pm 0.04$
$MeO(Me)CO$	16.60	0.22	$16.38 \pm 0.03$
$EtO(Me)CO$	17.32	0.24	$17.08 \pm 0.05$
$iPrO(Me)CO$	17.69	0.16	$17.53 \pm 0.05$
$EtO(Pr)CO$	16.85	0.09	$16.76 \pm 0.05$
$(MeO)_2CO$	15.32	0.15	$15.17 \pm 0.03$
$(EtO)_2CO$	16.31	0.33	$15.98 \pm 0.05$

proportional to the temperature increase. The obtained data are given in Table 3 together with the calculated values of the enthalpy change for the formation of the adducts in solution according to eqn. III.

### DISCUSSION

The discussion will be based on the ideas about the two reverse effects of substitution in carbonyl compounds as they have been developed in an earlier paper<sup>2</sup>. The replacement of an alkyl group by an alkoxy group was there assumed to influence the electron distribution in the donor molecule in two ways. The higher electronegativity of the alkoxy group should lead to an increased withdrawal of electrons from the carbonyl bond and thus decrease the donor strength, as observed with a greater number of other esters<sup>2</sup>. On the other hand the possible delocalization of a lone electron pair on the alkoxy

oxygen atom, corresponding to the electron distribution  $O^- - \overset{\text{R}}{\underset{\text{OR}^+}{\text{C}}}$  should

increase the electron density on the carbonyl oxygen atom and thus also the donor strength. It was pointed out that the two effects almost balanced each other in the comparison of ketones with esters, but the finer details were left to a quantitative study. This now shows that the direct replacement of a methyl group in acetone by a methoxy group in methyl acetate leads to a small decrease (0.65 kcal/mole) of the heat of reaction. The balance is thus almost perfect but the electronegativity effect might be slightly greater. (It does not seem profitable, however, to base any far-going conclusions on this small difference considering other possible differences between the two donor molecules.)

The effects of substitution in different acetates are also small but a trend is obvious and should be pointed out. The heat of reaction increases in the order methyl acetate, ethyl acetate and isopropyl acetate, which is the order of increasing electron repulsion of the alkyl group (+ I-effect)<sup>9</sup>. It is interesting to note that the increase in  $-\Delta H$ , when going from methyl- to ethyl-carbonate is only slightly larger than that between methyl- and ethyl-acetate.

The introduction of a second alkoxy group in the carbonates should almost double the "electronegativity" effect, while the "delocalization" effect should increase less considering that delocalization is already present in the acetate. The decrease in the heat of reaction, going from methyl acetate to dimethyl carbonate is also much larger than going from acetone to methyl acetate (1.22 kcal/mole compared with 0.64 kcal/mole).

The only comparison between esters of different acids which can be made is between ethyl acetate and ethyl butyrate, and here the heat of reaction of the butyrate is lower by 0.33 kcal.mole<sup>-1</sup>. Although this difference seems to be significant,<sup>10</sup> a discussion must await the determination of further data.

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