

## Enthalpies of Formation of Adducts between Antimony Pentachloride and Various Esters

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Enthalpies of formation of a number of donor-acceptor adducts have been determined with both reactants and reaction products in ethylene chloride solution. Using antimony pentachloride as the acceptor in all experiments, the heats of formation ( $-\Delta H$  kcal·mole<sup>-1</sup>) of the 1:1 addition compounds using the following esters were found as follows: ethyl formate [17.00], methyl trifluoroacetate [2.7], methyl propionate [16.23], methyl pivalate [12.83], isopropyl pivalate [13.5] and  $\gamma$ -butyrolactone [17.49].

The stability constants were determined for the addition compounds of antimony pentachloride and methyl pivalate [ $7801 \cdot \text{mole}^{-1}$ ] and methyl trifluoroacetate [ $0.6 \cdot \text{mole}^{-1}$ ].

The shift in carbonyl stretching frequency, caused by adduct formation, has been determined for methyl trifluoroacetate and  $\gamma$ -butyrolactone. The values found were 54 and 151 cm<sup>-1</sup>, respectively.

Results from investigations into adduct formation between antimony pentachloride and carboxylic esters have been reported in previous communications.<sup>1-3</sup> Earlier, enthalpies of formation values were given for adducts of different esters,<sup>1,2</sup> chosen to show the influence of alkyl substitution. Enthalpies of formation and stability constants of adducts with  $\alpha$ -methyl- and  $\alpha$ -chloro-substituted ethyl acetates have also been reported.<sup>3</sup> Additional data on ester adducts are given in this paper.

### EXPERIMENTAL \*\*

*Materials.* Ethylene chloride was treated as given in Ref. 1. The percentage of water impurity was determined as in a method reported previously<sup>4</sup> and found to be  $0.4 \pm 0.1$  mmole/charge. Antimony pentachloride was treated as described in Ref. 5. In measurements with methyl trifluoroacetate, Merck's antimony pentachloride for chromatography was used without further purification.

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\*\* Apparatus see Ref. 3; Calibration and Corrections to standard states see Ref. 1.

*Ethyl formate* (Fluka) was fractionally distilled. The sample was found to contain an impurity which could not be removed by distillation. By using GLC (dioctylphthalate on Celite and polyethyleneglycol 1000 on Chromosorb P) the impurity was identified as ethanol. Titration after alkaline hydrolysis indicated the amount of ethanol in the main fraction to be  $1.5 \pm 0.1\%$  by weight.

*Methyl trifluoroacetate*, *methyl propionate* and *methyl pivalate* (Fluka) were dried with Drierite and fractionally distilled. *Isopropyl pivalate* was synthesized from pivaloyl chloride and isopropyl alcohol. After washing with water and  $\text{NaHCO}_3$  solution the product was fractionally distilled under reduced pressure. Freshly regenerated micro-sieves were used to dry the sample.

$\gamma$ -*Butyrolactone* (Fluka) was fractionally distilled and the main fraction further purified by preparative GLC (Wilkins Autoprep, Carbowax 20 M on Chromosorb W). The sample was dried using micro sieves.

The purity of the esters was checked by analytical GLC (polyethyleneglycol 1000 as stationary phase on Chromosorb P) and by titration after alkaline hydrolysis \* which indicated  $99.9 \pm 0.1\%$  purity of the three first-mentioned esters and  $99.8 \pm 0.2\%$  of the latter two. Refractive indices (D-line) and relative densities of the samples at  $25^\circ\text{C}$  were *methyl trifluoroacetate*,  $n$  1.289,  $d$  1.2780; *methyl propionate*,  $n$  1.3750,  $d$  0.9093; *methyl pivalate*,  $n$  1.3879,  $d$  0.8690; *isopropyl pivalate*,  $n$  1.3870,  $d$  0.8289 and  $\gamma$ -*butyrolactone*,  $n$  1.4351,  $d$  1.1250.

*Ethanol* (99.5%) was used without further treatment. *Methyl acetate* was the same sample as used in Ref. 2.

The water content of the methyl trifluoroacetate and  $\gamma$ -butyrolactone samples was checked by a method using  $\text{CaH}_2$ <sup>7</sup> and was found to be less than 0.02% by weight in each sample. The sample of methyl pivalate was shown to contain  $0.09 \pm 0.02\%$  by volume water by gas chromatography using a Porapak Q column.<sup>8,9</sup> The apparatus was calibrated against a sample to which a known amount of water had been added.

*Calorimetric procedure.* The standard calorimetric procedure to determine enthalpies of adduct formation has been described elsewhere,<sup>1</sup> as have the simultaneous determinations of enthalpies and stability constants of adduct formation.<sup>3</sup>

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

Donor	mmole	g $\text{SbCl}_5$	$q$ cal	$-\Delta H$ kcal/mole
<i>Ethyl formate</i> $p = -0.06$	1.266	1.13	21.81	17.23
	1.824	1.35	31.46	17.25
	2.031	1.17	35.01	17.24
	2.732	1.38	46.90	17.17
				$17.22 \pm 0.02$
<i>Methyl propionate</i> $p = 0.00$	1.302	1.09	21.45	16.47
	1.474	1.10	24.22	16.43
	1.970	1.06	32.49	16.49
	2.473	1.11	40.61	16.42
	3.516	1.30	57.76	16.43
			$16.45 \pm 0.01$	
$\gamma$ - <i>Butyrolactone</i> $p = 0.03$	0.984	1.11	17.69	17.98
	1.144	1.18	20.62	18.02
	1.439	1.65	25.95	18.03
	1.446	1.18	26.02	18.00
			$18.01 \pm 0.01$	

\* For the hydrolysis of methyl and isopropyl pivalate see Ref. 6.

*Infrared measurements* were performed as described in Ref. 3.

*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. The molecular weights were computed from the 1961 Table of Atomic Weights.<sup>10</sup>

## RESULTS

The results of the heat measurements for the reactions where conversion is complete are summarized in Table 1. The first column indicates the donor together with a sum correction,  $p$  (in cal.), compensating for small heat effects arising from incompletely filled ampoules.<sup>11</sup> Columns 2 and 3 give the amounts of donor and acceptor and column 4 the corrected amount of heat evolved. The last column gives the molar enthalpy change.

The results of the calorimetric experiments on reactions with incomplete conversion to adduct are summarized in Table 2. The first column states the donor together with the calculated values of the enthalpy change and stability constant for the adduct formation reaction. Column 2 gives the amount of donor and column 3 the corrected amount of acceptor. The fourth column shows the corrected amount of heat evolved and the last column gives the heat evolved in cal.mole<sup>-1</sup> of donor corrected for heat of solution. The values where methyl pivalate was used are corrected for the presence of water in the sample (0.09 % by volume). It was assumed that all the water present reacts with SbCl<sub>5</sub> and gives a heat of reaction of -24.3 kcal/mole.<sup>4</sup>

The following equation has been derived for the relationship between the enthalpy of formation and the stability constant of 1:1 adducts:<sup>3</sup>

$$(-\Delta H)^2 + \Delta H \cdot h \left( 1 + \frac{d}{a} + \frac{V}{a \cdot K} \right) + \frac{h^2 \cdot d}{a} = 0 \quad (1)$$

$\Delta H$  is the molar enthalpy change and  $K$  the stability constant,  $d$  and  $a$  are the amounts of donor and acceptor and  $V$  the total volume of solution.  $h$  is the heat evolved, corrected for heat of solution, in an experiment where an unknown amount of adduct is formed. The  $\Delta H$  and  $K$  values of methyl pivalate were found by minimizing the square sum of eqn. 1 for a network of  $\Delta H$  and  $K$  values. The error limits, expressed as the standard deviations of the means have been estimated as described in Ref. 3. The  $\Delta H$  and  $K$  values of methyl trifluoroacetate were found by inserting the experimental data in eqn. 1 and solving the equation systems obtained. The heat of reaction between isopropyl pivalate and SbCl<sub>5</sub> could not be determined accurately due to interfering side reactions which impeded the determination of the stability constant. The after periods indicated the presence of a weakly endothermic reaction which, after a few minutes, was followed by a slow exothermic process. It was found from experiments on other systems that the addition reaction was almost complete within 1.5 min. The values of the heat of reaction of isopropyl pivalate given in Table 2 have been calculated using 1.5 min as the length of the main period. From a consideration of the derived heat of reaction values, the stability constant of the SbCl<sub>5</sub>-isopropyl pivalate adduct should amount to at least 2300 l/mole, which is the value of the ethyl pivalate adduct.<sup>3</sup> The enthalpy value reported for complete conversion to

Table 2. Heat of reaction measurements in ethylene chloride solution where an unknown amount of adduct was formed.

Donor	mmole	mmole SbCl <sub>5</sub>	q cal	h cal/mmole
Methyl trifluoroacetate	1.373	32.9	-0.79	0.44
-ΔH = 2.7 ± 0.4 kcal/mole	2.886	34.3	-1.69	0.42
K = 0.6 ± 0.1 l/mole	2.889	67.2	-0.73	0.76
	3.344	67.2	-0.88	0.75
Methyl pivalate	0.979	3.64	12.08	12.25
	0.847	3.65	10.48	12.27
-ΔH = 12.83 ± 0.02 kcal/mole	1.868	3.72	22.65	12.03
K = 780 ± 40 l/mole	2.213	4.61	27.10	12.15
	1.137	7.10	14.44	12.60
	0.921	7.45	11.66	12.58
	0.962	7.89	12.16	12.54
Isopropyl pivalate	0.768	2.81	9.74	13.10
	0.935	3.50	11.82	13.06
-ΔH = 13.5 ± 0.1 kcal/mole	1.823	2.65	23.19	13.14
	2.120	2.81	26.85	13.08

adduct has been calculated assuming a value for the stability constant of 2500 l/mole.

The heat of solution measurements (Table 3) were performed in pure ethylene chloride.

Summaries of the determinations, together with some previously reported data, are given in Tables 4 and 5. In Table 4 the first column shows the formula of the donor and the second the heat of reaction between liquid donor and SbCl<sub>5</sub> in ethylene chloride solution. The heat of solution of the donor is given in the third column and the fourth gives the calculated value of the enthalpy change for the reaction with both reactants and reaction product in ethylene chloride solution. The enthalpy of adduct formation of ethyl formate has been corrected for the presence of 1.5 % ethanol in the sample. The heat of reaction between ethanol and SbCl<sub>5</sub> was found to be 17.9 ± 0.5 kcal·mole<sup>-1</sup> from measurements on an ethyl formate solution containing additional ethanol (11.8 % by weight).

In Table 5 the first column shows the formula of the donor. Columns 2 and 3 give the enthalpy change for adduct formation and stability constant of the adduct, respectively. The calculated values of the free energy and entropy changes are given in columns 4 and 5. These thermodynamic quantities refer to the addition reaction with both reactants and reaction product in ethylene chloride solution. The uncertainties are the standard deviations of the mean. An assessment of the errors due to uncertainty in the estimated *K* value and of the influence of side reactions have been included in the uncertainty of the Δ*H* value of isopropyl pivalate. The error limits given for the enthalpy and stability constant values of methyl pivalate and methyl trifluoroacetate include allowances for uncertainties in water content of the calorimetric liquid and donor samples.



Table 5. Thermodynamic quantities for the formation of adducts between  $\text{SbCl}_5$  and different donors in ethylene chloride solution.

Donor	$-\Delta H$ kcal · mole <sup>-1</sup>	$K$ l · mole <sup>-1</sup>	$-\Delta G^b$ kcal · mole <sup>-1</sup>	$-\Delta S$ e.u.
$\text{CH}_3\text{O}(\text{CF}_3)\text{CO}$	2.7 ± 0.4	0.6 ± 0.1	-2.2 ± 0.1	16.4 ± 1.4
$\text{C}_2\text{H}_5\text{O}(\text{CCl}_3)\text{CO}^a$	3.05 ± 0.07	1.7 ± 0.2	-1.60 ± 0.06	15.6 ± 0.3
$\text{CH}_3\text{O}(t\text{-C}_4\text{H}_9)\text{CO}$	12.83 ± 0.06	780 ± 80	2.05 ± 0.06	36.2 ± 0.3
$\text{C}_2\text{H}_5\text{O}(t\text{-C}_4\text{H}_9)\text{CO}^a$	13.03 ± 0.04	2300 ± 100	2.69 ± 0.04	34.7 ± 0.2
$i\text{-C}_3\text{H}_7\text{O}(t\text{-C}_4\text{H}_9)\text{CO}$	13.5 ± 0.3			

<sup>a</sup> From Ref. 3.

<sup>b</sup> Computed from  $K$  in atm<sup>-1</sup>.

The infrared spectra measurements of methyl trifluoroacetate were performed using ethylene chloride solutions, 0.03 M in ester and 0.7 M in  $\text{SbCl}_5$ . The  $\gamma$ -butyrolactone and methyl acetate solutions were 0.02 M in donor and 0.05 M in  $\text{SbCl}_5$ . The results of the infrared measurements are given in Table 6. The first column shows the donor and columns 2 and 3 give the carbonyl stretching frequencies of the free donor and of the adduct, respectively. The last column indicates the shift in frequency caused by adduct formation. Data for two previously reported esters have been included in Table 6.

## DISCUSSION

The influence of alkyl substitution, in the alkyl or alkoxy groups attached to the carbonyl group, on the enthalpy of adduct formation has been discussed in previous communications.<sup>2,3</sup> It was noticed that methyl substitution in the alkyl group resulted in a decrease in the  $-\Delta H$  values while substitution in the alkoxy group led to an increase. The latter observation was based on enthalpy of formation values of  $\text{SbCl}_5$  adducts with methyl, ethyl, and isopropyl acetate as donors. The positive inductive effect of methyl substitution is also found in the propionic esters, the  $-\Delta H$  value of ethyl propionate<sup>2</sup>

Table 6. Infrared spectra measurements of the carbonyl stretching frequency in the free donors and in  $\text{SbCl}_5$  adducts.

Donor	Carbonyl stretching frequency cm <sup>-1</sup>		shift cm <sup>-1</sup>
	free donor	adduct	
$\text{CH}_3\text{O}(\text{CF}_3)\text{CO}$	1782	1728	54 ± 8
$\text{CH}_3\text{O}(\text{CH}_3)\text{CO}$	1735	1580	155 ± 7
$\text{C}_2\text{H}_5\text{O}(\text{CH}_3)\text{CO}^a$	1725	1565	160 ± 6
$\text{C}_2\text{H}_5\text{O}(\text{CCl}_3)\text{CO}^a$	1757	1683	74 ± 6
$\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CO}$  -----  O	1766	1615	151 ± 6

<sup>a</sup> From Ref. 3.

being  $0.6 \text{ kcal}\cdot\text{mole}^{-1}$  higher than that of the methyl ester. The effect is less pronounced in the pivalates. It is noticed that, while the  $\Delta H$ -values for methyl and ethyl pivalate differ by  $0.2 \text{ kcal/mole}$ , the difference between their  $\Delta G$ -values is  $0.6 \text{ kcal/mole}$ , which implies a difference in the entropy change upon adduct formation of  $1.5 \text{ e.u.}$

Within the limits of experimental error ethyl formate gave the same enthalpy of adduct formation as ethyl acetate. The hydrogen atom would be expected to exert a negative inductive effect and reduce the donor power of the carbonyl oxygen atom, as it is ascribed a  $\sigma^*$ -value of  $+0.49$ , as compared to the value zero (by definition) for the methyl group.<sup>12</sup> It is possible that the smaller steric hindrance of the hydrogen atom counterbalances the presumed negative inductive effect.

The difference between the  $\Delta H$ -values of methyl acetate and methyl trifluoroacetate is  $13.7 \text{ kcal/mole}$ . The exchange of three fluorine for three hydrogen atoms in dimethylacetamide ( $\Delta H = -27.80 \text{ kcal/mole}$ ) to give dimethyltrifluoroacetamide results in a lowering of the  $\Delta H$ -value by  $11.2 \text{ kcal/mole}$ .<sup>4</sup> It thus seems that the ester is more susceptible to the effect of strongly electronegative substituents than the amide.

The shift in the carbonyl stretching frequency of methyl trifluoroacetate, caused by adduct formation, was found to be  $54 \text{ cm}^{-1}$ . A shift of this magnitude agrees satisfactorily with the plot of frequency shift against enthalpy of adduct formation for  $\alpha$ -methyl- and  $\alpha$ -chlorosubstituted ethyl acetates.<sup>3</sup> It was concluded that the shifts in carbonyl frequency could be used to estimate the relative donor strengths of these closely related species. On the other hand the shift of propionyl chloride has been shown to be  $197 \text{ cm}^{-1}$  and the enthalpy of adduct formation only  $-3.3 \text{ kcal/mole}$ , which shows that the donor strength of this compound cannot be estimated from its frequency shift.<sup>13</sup> The rather large shifts for  $\text{CCl}_3\text{COOEt}$  and  $\text{CF}_3\text{COOMe}$ , of  $74$  and  $54 \text{ cm}^{-1}$ , respectively, while the heat of formation values of the adducts are small, may seem at first surprising. There are, however, at least two possible reasons for this behaviour. Firstly, the enthalpy of adduct formation includes the energy of rehybridization of the acceptor in addition to the enthalpy of formation of the donor-acceptor bond (*cf.* Ref. 14). The first effect is probably endothermic and counterbalances the energy liberated by the adduct formation reaction. The "bonding" energy between the donor and acceptor can be considerably larger than the  $\Delta H$ -value indicates. Secondly, it is possible that the structures of the adducts are different for strong and weak interaction between donor and acceptor, although the donors are similar types of compound.

In the 5-membered ring compound  $\gamma$ -butyrolactone, the bond angle, within the ring, at the carbonyl-carbon is reduced by about  $10^\circ$  from the theoretical value  $120^\circ$ . This reduction in the bond angle does not introduce any appreciable amount of strain energy.\* However, the rehybridization of the carbonyl carbon, which accompanies the reduction in bond angle, effects the carbonyl stretching frequency and presumably introduces more *s*-character to the carbonyl bond.<sup>16</sup> The carbonyl group in 5-membered ring compounds has been found to exhibit absorption maxima at a frequency approximately

\* *Cf.* discussion of the strain energy in methylene cyclopentane in Ref. 15.

40 wave numbers higher than the straight chain compound.<sup>16</sup> The difference between butyrolactone and ethyl acetate determined by this investigation was  $41\text{ cm}^{-1}$ . Increased *s*-character of the carbonyl carbon hybrid would be expected to lower the donor ability of the carbonyl oxygen, since the carbon atom apparently becomes more electronegative.<sup>17</sup> This expected lowering in the donor strength of butyrolactone was, however, not revealed by the enthalpy of adduct formation with  $\text{SbCl}_5$  as acceptor. The  $-\Delta H$  value of  $\gamma$ -butyrolactone was found to be 17.49 kcal/mole which is comparable with the value of ethyl acetate (17.08 kcal/mole).<sup>1</sup> The carbonyl stretching frequency shifts caused by adduct formation were, within the limits of experimental error, the same for both donors. Presumably the inductive effect of the alkyl groups in ethyl acetate and in butyrolactone are the same. In the lactone, the alkoxy and the carbonyl groups are forced into a *trans*-configuration, whereas they have been shown<sup>18</sup> to exist in a *cis*-configuration in aliphatic esters. The slightly higher heat of adduct formation of butyrolactone is perhaps due to the fact that in the lactone the carbonyl oxygen has the opportunity of coordinating with the acceptor with a minimum of steric hindrance.

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