

Enthalpies of Formation and Stability Constants for Adducts between Antimony Pentachloride and Substituted Ethyl Acetates

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Enthalpies of formation and stability constants have been determined calorimetrically in ethylene chloride solution for electron donor-acceptor adducts between antimony pentachloride and six chlorine- and methyl-substituted ethyl acetates. The following results were obtained: the enthalpy of formation ($-\Delta H$) values are given in kcal-mole⁻¹ and the stability constants, given within brackets, in l-mole⁻¹; ethyl monochloroacetate: 12.80 [3.8×10^3], ethyl dichloroacetate: 9.35 [49], ethyl trichloroacetate: 3.05 [1.7], ethyl propionate: 16.82 [3.0×10^6], ethyl isobutyrate: 16.37 [8.8×10^6] and ethyl pivalate: 13.03 [2.3×10^3].

The shifts in the infrared stretching frequency of the carbonyl group in the ethyl acetates caused by adduct formation with antimony pentachloride have been determined. The infrared measurements were made on ethylene chloride solutions and the following results were obtained: shifts are given in cm⁻¹; ethyl acetate: 160; ethyl propionate: 162; ethyl isobutyrate: 155; ethyl pivalate: 137; ethyl monochloroacetate: 150; ethyl dichloroacetate: 116; and ethyl trichloroacetate: 74.

In previous communications the determinations of the enthalpy of adduct formation between some alkylcarboxylates and antimony pentachloride have been reported.^{1,2} This paper gives data for the ethyl esters of the chlorine substituted acetic acids to show the influence of inductive effects on the enthalpy of adduct formation. The enthalpy values for the α -methyl substituted ethyl acetates have been redetermined, and it has been possible to determine the stability constants for the adduct formation reaction for all six esters.

The effect of α -substitution on the donor properties of aliphatic esters has previously been investigated by Bystrov³ and Jain and Rivest.⁴ The authors studied the infrared spectra of the free esters and of their adducts with different metal halides as electron acceptors.

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To be able to compare the enthalpy of formation values obtained here with infrared shifts in carbonyl stretching frequencies between the free esters and adducts with antimony pentachloride, spectra were taken on ethylene chloride solutions of the same concentration as used in the calorimetric measurements.

EXPERIMENTAL

Materials. Ethylene chloride was treated as given in Ref. 1 and antimony pentachloride as in Ref. 5. In the experiments with 0.3 M and 0.7 M solutions Merck's antimony pentachloride for chromatography was used without further treatment.

The ethyl chloroacetates (Fluka) were distilled under reduced pressure after drying with Drierite. The purity of the esters was checked by analytical GLC using polyethyleneglycol 1000 as stationary phase on Chromosorb P, and by titration after alkaline hydrolysis which indicated 100.1 ± 0.1 % purity for all three esters.

Ethyl monochloroacetate	n_D^{25} 1.4192	d_4^{25} 1.1443
Ethyl dichloroacetate	n_D^{25} 1.4363	d_4^{25} 1.2762
Ethyl trichloroacetate	n_D^{25} 1.4482	d_4^{25} 1.3767

Ethyl propionate (Schueckardt) was fractionally distilled after drying with Drierite. Purity was checked by analytical GLC with dioctylphthalate as stationary phase on Chromosorb P, and by titration after alkaline hydrolysis which indicated 99.9 ± 0.1 % purity. n_D^{25} 1.3821.

Ethyl isobutyrate (Fluka) was fractionally distilled and the main fraction further purified using preparative GLC (Wilkins Autoprep, Carbowax 20 M on Chromosorb W). Impurities could not be detected by analytical GLC using polyethyleneglycol 1000, and apiezon on Chromosorb P, dioctylphthalate on Celite and carbowax 1500 on Chromosorb G as stationary phases. The sample was dried with CaH_2 immediately before use. n_D^{25} 1.3852.

Ethyl pivalate was the same sample as in Ref. 2. A pure sample of ethyl acetate was supplied by Dr. I. Wadsö at this laboratory.

The water content of the esters (except ethyl acetate) was checked by gas chromatography using a Porapak Q column.^{6,7} The three chloroesters and ethyl isobutyrate were shown to contain less than 0.01 % (vol) of water. The water content of ethyl propionate was 0.02 ± 0.01 % and of ethyl pivalate 0.11 ± 0.02 % (vol). The apparatus was calibrated using water saturated octane, and in the determination of the water content of ethyl pivalate by preparing a sample with a known amount of water added to the original sample.

Apparatus. Calorimetric equipment, see Ref. 1. The stop watch used to measure the calibration time has been replaced by an electronic time-measuring device.

The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. Cells with Irtran-2 windows and 1 mm Teflon spacers were used for the measurements.

Calibration. See Ref. 1. The calibration time varied from 60 to 240 sec and no significant difference between the heat equivalent values with long and short calibration times could be detected.

Calorimetric procedure. For the simultaneous determinations of ΔH and K the calorimeter was charged with 101.6 ml of ethylene chloride and 3–10 mmoles of SbCl_5 . At higher concentrations of SbCl_5 the volume of ethylene chloride was 100.6 ml and 94.6 ml and the amount of SbCl_5 33 and 66 mmoles, respectively.

In the substitution reaction measurements the amount of SbCl_5 -ethyl monochloroacetate adduct available was determined by measuring the heat evolved when an ampoule with 7–8 mmoles of ethyl chloroacetate was broken in the system containing 2–3 mmoles SbCl_5 in 101.6 ml ethylene chloride. The ampoule with the second donor (ethyl propionate or ethyl isobutyrate) was then introduced into the system.

The reactions took place instantaneously and the reaction period was in all cases less than 4 min, and no side reactions could be detected. The initial and final resistance values were obtained graphically. In the determinations with ethyl monochloroacetate as donor the expression $\log R_i - \log R_f / \log R_i \times \log R_f$ was used as being proportional to ΔT and in the other determinations $(R_i - R_f)/(R_i + R_f)$ was used.⁸

Infrared measurements were performed on ethylene chloride solutions with pure ethylene chloride in the reference cell. Spectra of the free esters were run on 0.02 M solutions and of the adducts on solutions that were 0.02 M in donor and 0.05 M in SbCl_5 . Ethyl di- and trichloroacetate were also measured in 0.5 M SbCl_5 solution. The same shift was obtained at both concentrations for the dichloroester while the ethyl trichloroacetate- SbCl_5 adduct was formed in measurable quantities only in the 0.5 M solution. In these dilute solutions, due to the absorption of the solvent, the carbonyl stretching frequency was the only one that could be studied. Blank experiments were run on the SbCl_5 solutions. No absorption interfering with that of the carbonyl group was found.

Corrections to standard states. See Ref. 1.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie equal to 4.1840 abs.joules. Given thermodynamic data 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.⁹

RESULTS

Due to the availability of better calorimetric equipment it has now been possible to determine the variation of the heat evolved per mole of donor with varying concentrations of donor and acceptor and thus to determine the stability constant for the adduct formation reaction. This could be done even in cases where the degree of conversion varied only a few percent in the concentration region that could be used.

The following equation was derived for the simultaneous determination of the enthalpy of adduct formation and the stability constant:*

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

In eqn. 1 ΔH represents the molar enthalpy change in $\text{cal} \cdot \text{mmole}^{-1}$, equal to $\text{kcal} \cdot \text{mole}^{-1}$, and K the stability constant in $\text{ml} \cdot \text{mmole}^{-1}$ equal to $\text{l} \cdot \text{mole}^{-1}$ for the adduct formation reaction with both reactants and reaction product in ethylene chloride solution. h is the heat evolved per mmole of donor in an experiment, corrected for heat of solution. V is the total volume of the solution in ml, d is the amount of donor in mmoles and a is the amount of antimony pentachloride in mmoles.

The amount of water in the ethylene chloride used in the determinations with the ethyl chloroacetates as donors was estimated by a method using calcium hydride¹² and was found to be 0.5 ± 0.2 mmole/100 ml. The total amount of water in the calorimeter vessel charged with ethylene chloride used in the determinations with ethyl pivalate as donor was determined by measuring the heat evolved when an ampoule of SbCl_5 was broken in the system. It was found to be 0.4 ± 0.1 mmole. The enthalpy of adduct formation between antimony pentachloride and water has been determined to $-24.3 \text{ kcal} \cdot \text{mole}^{-1}$.¹³ It is assumed that the adduct with water is so strong that no conversion will occur when the donors are added.

* For earlier reported determinations of stability constants from calorimetric measurements on adduct formation reactions see, e.g., Bolles and Drago¹⁰ and Nelander.¹¹

To solve eqn. 1 the minimum of

$$\sum_{i=1}^n (-\Delta H)^2 + \Delta H \cdot h_i \left(1 + \frac{d_i}{a_i} + \frac{V_i}{a_i \cdot K} \right) + \frac{h_i^2 d_i}{a_i} \quad (2)$$

(n is the number of experiments)

was determined from a network of ΔH and K values.* For ethyl monochloroacetate and ethyl pivalate ΔH could also be obtained directly from the experiments with high concentration of SbCl_5 . The agreement between the values obtained by the two methods was satisfactory.

Table 1. Heat of reaction measurements performed in ethylene chloride solution containing an excess of SbCl_5 as acceptor.

Donor	mmole	mmole SbCl_5	q cal	h cal- mmole ⁻¹	
Ethyl monochloroacetate	1.731	3.52	21.93	12.60	
	1.506	3.08	19.07	12.59	
	1.066	3.58	13.58	12.67	
	1.271	4.28	16.22	12.69	
	1.700	4.46	21.66	12.67	
	1.534	11.38	19.73	12.79	
	1.627	33.7	20.89	12.77	
	0.759	33.2	9.76	12.79	
	1.217	33.2	15.64	12.78	
	$-\Delta H = 12.80 \pm 0.01$ kcal-mole ⁻¹ $K = 3750 \pm 70$ l-mole ⁻¹				
Ethyl dichloroacetate	1.143	9.58	8.52	7.54	
	0.971	10.24	7.25	7.55	
	1.650	5.13	9.92	6.10	
	1.520	4.60	8.94	5.97	
	2.106	4.53	11.75	5.66	
	1.155	6.80	7.89	6.91	
	1.390	8.47	10.01	7.28	
	1.153	9.52	8.65	7.59	
	$-\Delta H = 9.35 \pm 0.05$ kcal-mole ⁻¹ $K = 49 \pm 1$ l-mole ⁻¹				
	Ethyl trichloroacetate	0.939	4.59	0.07	0.22
0.958		4.55	0.06	0.20	
1.226		32.9	1.21	0.98	
1.709		33.4	1.46	1.00	
0.753		66.9	1.18	1.71	
2.118		66.2	3.28	1.70	
$-\Delta H = 3.05 \pm 0.05$ kcal-mole ⁻¹ $K = 1.7 \pm 0.1$ l-mole ⁻¹					
Ethyl pivalate	0.901	3.75	11.59	12.83	
	1.947	3.55	24.73	12.67	
	1.553	3.31	19.78	12.71	
	1.485	3.18	18.94	12.72	
	1.461	33.5	19.06	13.01	
	2.381	33.2	31.05	13.01	
	$-\Delta H^a = 13.03 \pm 0.01$ kcal-mole ⁻¹ $K = 2300 \pm 40$ l-mole ⁻¹				

^a The value given in Ref. 2 (12.93 ± 0.03 kcal/mole) refers to about 98 % conversion of ester to adduct. The value for complete conversion is about 0.2 kcal/mole higher than the value here. The discrepancy is probably due to water not corrected for in the sample used in the earlier determinations.

* For the calculations SMIL, electronic computer of the University of Lund, was used.

The experimental results are summarized in Tables 1 and 2. In Table 1 the first column gives the name of the donor and the calculated values of ΔH and K . Columns 2 and 3 give the amount of donor and corrected amount of acceptor. Column 4 gives the heat evolved in the experiment corrected for small heat effects due to incompletely filled ampoules.⁸ The last column gives the heat evolved per mmole of donor with an unknown amount of adduct formed. The values for ethyl pivalate are corrected for the presence of 0.11 % (vol) water in the sample, assuming that all the water present reacts with SbCl_5 .

The error limits given for ΔH and K , and expressed as standard deviations of the means, were estimated from the individually calculated values of ΔH or K when the other parameter, *i.e.* K or ΔH , was constant and equal to the value obtained from the minimization of (2).

Heat of solution experiments (Table 2) were performed in pure ethylene chloride. The values for the heats of solution of ethyl propionate, ethyl isobutyrate and ethyl pivalate were taken from Ref. 2.

The enthalpies of adduct formation for ethyl propionate and ethyl isobutyrate were redetermined and the $-\Delta H$ values obtained were 16.82 ± 0.01 and 16.37 ± 0.02 kcal·mole⁻¹, respectively. A correction was applied for the presence of 0.02 % (vol.) of water in the ethyl propionate sample. The values reported in Ref. 2 are 16.82 ± 0.03 kcal·mole⁻¹ for ethyl propionate and 16.44 ± 0.05 for ethyl isobutyrate. The latter value had not been corrected for heat of solution, however, and the correct value should have been 16.41 kcal·mole⁻¹.

The stability constants for the adduct formation reaction with ethyl propionate and ethyl isobutyrate as donors cannot be determined directly due to complete conversion to adduct in the concentration region used. Instead the equilibrium constant can be determined for a substitution reaction.



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

Donor	mmole	q cal	$-\Delta H$ kcal/mole
Ethyl monochloroacetate	1.771	0.12	0.07
	2.430	0.16	0.07
	2.964	0.21	0.07
			0.07 ± 0.00
Ethyl dichloroacetate	1.822	-0.16	-0.09
	2.152	-0.17	-0.08
	2.418	-0.21	-0.09
			-0.09 ± 0.00
Ethyl trichloroacetate	1.641	-0.23	-0.14
	2.234	-0.33	-0.15
	2.325	-0.36	-0.15
			-0.15 ± 0.00

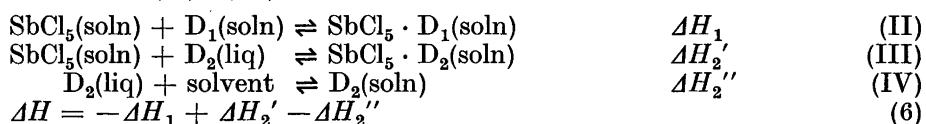
$$K = \frac{[\text{SbCl}_5 \cdot \text{D}_2] \cdot [\text{D}_1]}{[\text{SbCl}_5 \cdot \text{D}_1] \cdot [\text{D}_2]} \quad (3)$$

$$K_1 = \frac{[\text{SbCl}_5 \cdot \text{D}_1]}{[\text{SbCl}_5] [\text{D}_1]} \quad (4)$$

Multiplying (3) by (4) gives

$$K \cdot K_1 = K_2 = \frac{[\text{SbCl}_5 \cdot \text{D}_2]}{[\text{SbCl}_5] [\text{D}_2]} \quad (5)$$

In the above reaction and equations D_1 represents ethyl monochloroacetate and D_2 ethyl propionate or ethyl isobutyrate. K is the equilibrium constant for the substitution reaction and K_1 the stability constant for the ethyl monochloroacetate adduct formation reaction. K_2 is the stability constant to be determined for the adduct formation with ethyl propionate or ethyl isobutyrate as donors. The enthalpy change, ΔH , for reaction (I) can be obtained from reactions (II)–(IV)



The $-\Delta H$ values were found to be 4.02 ± 0.01 and 3.57 ± 0.02 kcal/mole for ethyl propionate and ethyl isobutyrate, respectively.

Table 3. Results of substitution reaction experiments in which $\text{CH}_2\text{ClCOOEt}$ in adduct with SbCl_5 is replaced by EtCOOEt or $i\text{-PrCOOEt}$.

Donor	mmole donor	mmole adduct	mmole ethyl monochloroacetate	q cal	α	K	
EtCOOEt	2.005	2.247	7.672	8.37	0.970	767	
	1.924	2.198	7.330	8.10	0.978	986	
	2.119	2.251	7.765	8.76	0.962	876	
	2.461	2.409	8.168	9.87	0.951 ^a	944	
	(3.0 \pm 0.3)10 ⁶	2.542	2.592	8.133	10.25	0.937	544
l·mole ⁻¹	1.994	2.175	8.157	8.32	0.966	690	
						801 \pm 71	
<i>i</i> -PrCOOEt	2.015	2.558	8.251	7.08	0.954	247	
	1.615	1.680	7.388	5.20	0.876	184	
	2.028	2.354	8.016	6.92	0.928	202	
	(8.8 \pm 1.2)10 ⁵	1.889	2.765	8.572	6.82	0.973	305
	l·mole ⁻¹						234 \pm 29

^a In this experiment the ester is in excess. The degree of conversion is instead computed from the amount of adduct.

The degree of conversion, α , in an experiment can be determined from the heat evolved, f , per mole of donor D_2 added to the calorimetric liquid containing an excess of $SbCl_5 \cdot D_1$ adduct. f is corrected for the heat of solution of the donor.

$$f = -\alpha \cdot \Delta H \quad (7)$$

K is then calculated considering the concentrations of all species involved in the reaction.

The results of the substitution reaction experiments are summarized in Table 3. The formula of the donor is given in the first column together with the calculated values of the stability constant for the adduct formation with antimony pentachloride. Column 2 gives the amount of donor, column 3 the amount of $SbCl_5 \cdot$ ethyl monochloroacetate adduct present in the calorimetric liquid, and column 4 the total amount of ethyl monochloroacetate. The fifth column gives the heat evolved in the substitution reaction and the sixth the degree of conversion. The last column gives the calculated values for the equilibrium constant for the substitution reaction.

The results of the calorimetric experiments together with the calculated values of the free energy and entropy changes are summarized in Table 4. The thermodynamic quantities refer to the adduct formation reaction with both reactants and reaction product in ethylene chloride solution. The ΔG values are computed from K -values expressed in atm^{-1} , ($K_p \times 24.46 = K_c$). The error limits given for the enthalpy and stability constant values include estimates of errors due to uncertainties in water content of the calorimetric liquid and donor samples.

The results of the infrared measurements are summarized in Table 5. The first column gives the formula of the donor. The second and third columns give the carbonyl frequency of the free ester (see Discussion) and of ester adduct, respectively. The last column gives the shift caused by adduct formation. The error limits for the frequency values are estimated to be $\pm 3 \text{ cm}^{-1}$ for the free esters and $\pm 6 \text{ cm}^{-1}$ for the adducts.

The adduct formation is accompanied by a broadening of the peaks and an increase in the total intensity of the carbonyl absorption bands (see, *e.g.*, Ref. 3).

Table 4. Thermodynamic quantities for the formation of adducts between $SbCl_5$ and substituted ethyl acetates ($R_iCH_{3-i}COOEt$) in ethylene chloride solution.

R	i	$-\Delta H$ kcal·mole ⁻¹	K l·mole ⁻¹	$-\Delta G^a$ kcal·mole ⁻¹	$-\Delta S$ e.u.
Me	1	16.82 ± 0.01	(3.0 ± 0.7) 10 ⁶	6.94 ± 0.15	33.1 ± 0.5
	2	16.37 ± 0.02	(8.8 ± 2.6) 10 ⁵	6.21 ± 0.20	34.1 ± 0.6
	3	13.03 ± 0.04	(2.3 ± 0.1) 10 ³	2.69 ± 0.04	34.7 ± 0.2
Cl	1	12.80 ± 0.01	(3.8 ± 0.5) 10 ³	2.98 ± 0.07	32.9 ± 0.2
	2	9.35 ± 0.05	(4.9 ± 0.2) 10 ¹	0.41 ± 0.03	30.0 ± 0.2
	3	3.05 ± 0.07	(1.7 ± 0.2) 10 ⁰	-1.60 ± 0.06	15.6 ± 0.3

^a Computed from K in atm^{-1} .

Table 5. Results of the infrared measurements of substituted ethyl acetates ($R_i\text{CH}_2\text{-COOEt}$) as free esters and in adducts with SbCl_5 in ethylene chloride solution.

R	<i>i</i>	Carbonyl stretching frequency (cm^{-1})		Shift cm^{-1}
		free ester	adduct	
Me	0	1725	1565	160
	1	1722	1560	162
	2	1720	1565	155
	3	1712	1575	137
Cl	1	{1749 1732	1582	150
	2	{1755 1738	1622	116
	3	1757	1683	74

DISCUSSION OF RESULTS

The carbonyl group in an aliphatic ester can be described as a sp^2 -hybridized carbon atom that forms one σ - and one π -bond to an oxygen atom. The remaining lone-pair electrons at the oxygen atom lie in the same plane as the $-\text{C}-\text{CO}-\text{O}-\text{C}-$ moiety. The two electron pairs are in different environments. On one side there is the alkyl group and on the other the alkoxy group. Therefore, the acceptor molecule has in principle two different sites to choose between for coordination.

In the free ester molecule the $\text{O}-\text{C}_{\text{alk}}$ bond is *cis* to the carbonyl bond¹⁴ and the same configuration of the ester molecule is found in the adduct ($\text{TiCl}_4 \cdot \text{CH}_3\text{COOC}_2\text{H}_5$)₂¹⁵ which is the only structure of an ester molecular adduct known to the author. It seems reasonable to assume the same ester configuration in adducts with antimony pentachloride in solution. The acceptor molecule will then coordinate at the free electron pair on the carbonyl oxygen that is on the same side as the alkyl group to avoid steric interaction with the alkoxy group. This is the case in the structure of the TiCl_4 -ethyl acetate adduct which was mentioned previously. This choice of coordination site will give rise to steric interaction when substituents are introduced at the carbon atom next to the carbonyl group. For the mono- and disubstituted acetates there will still be an α -hydrogen atom left that may occupy the position *cis* to the carbonyl bond and an adduct could form which is free from direct steric interactions between the acceptor molecule and the substituents. The alkyl group is probably hindered in its rotation round the $\text{C}-\text{C}_{\text{carboxyl}}$ bond in the adduct. In the α,α,α -substituted ethyl acetates model studies suggest direct steric interaction between the ester molecule and the chlorine atoms in antimony pentachloride independent of which of the sites is preferred for coordination.

For α -methyl substituted ethyl acetates the results from Ref. 2 have been confirmed. Increased α -branching gives a steady decrease in the $-\Delta H$ values from 17.08 kcal/mole for ethyl acetate to 16.37 kcal/mole for ethyl isobutyrate. This is contrary to the effect of methyl branching in the alkoxy group where an increase in the $-\Delta H$ values from 16.38 kcal/mole for methyl acetate to

17.53 kcal/mole for isopropyl acetate is found.¹ This different behaviour of the methyl group as substituent in the alkoxy group or at the α -carbon atom is also revealed by NMR measurements of the chemical shift of the methyl protons in acetate esters, $\text{CH}_3\text{COOR}'$ and in methyl esters, RCOOCH_3 .¹⁶ For acetates, branching in the alkoxy group leads to changes in the chemical shifts relative to that of methyl acetate that are -0.9 for C_2H_5 , -2.5 for $i\text{-C}_3\text{H}_7$ and -5.5 for $t\text{-C}_4\text{H}_9$ (cps at 37°C). The corresponding shifts in the methyl esters for branching in the α -position to the carbonyl carbon are $+0.7$, 0.8 , and 0.8 cps, respectively. Methyl groups in the alkoxy group seem to have an electron releasing effect while methyl groups at the α -carbon behave as if they were weakly electron withdrawing. From the results above it can be expected that ethyl pivalate should not differ much from ethyl propionate and isobutyrate in donor strength. The $-\Delta H$ value found is 13.03 kcal/mole, however, and this large decrease is probably mainly due to direct steric interaction between the donor and acceptor molecules.

It seems reasonable to compare the α -chlorine substituted ethyl acetates with the α -methyl substituted esters since the chlorine atom and the methyl group can be assigned almost the same size, van der Waals radii of 1.8 ± 0.1 and 2.0 ± 0.1 Å, respectively.¹⁷ The steric effect of chlorine substitution can then be accounted for by making a comparison with the corresponding methyl substituted ester. It is assumed that apart from the inductive effect of the substituents other effects in operation in the adduct formation reaction are the same for the chlorine substituted as for the methyl substituted ethyl acetates. The possible inductive effect of the methyl group is in any case small and it may be neglected in comparison with the effect of the chlorine atom. With these assumptions the inductive effect of the introduction of the first chlorine atom is a lowering of the $-\Delta H$ value by 4.0 kcal/mole (ethyl propionate *versus* ethyl monochloroacetate). The effect on the $-\Delta H$ value of introducing two chlorine atoms is 7.0 kcal/mole (ethyl isobutyrate *versus* ethyl dichloroacetate). The difference in the enthalpy of formation values between ethyl pivalate and ethyl trichloroacetate is 10.0 kcal/mole. If these $\Delta\Delta H$ values are plotted *versus* Taft's σ^* values for the chloromethyl groups¹⁸ a good linear relation is obtained (Fig. 1).

As may be seen from the results in Table 4 there is no linear entropy-enthalpy relation (see, *e.g.*, Ref. 19) in this series of adducts. The entropy changes for adduct formation, with the exception of ethyl trichloroacetate as donor, are rather insensitive to enthalpy changes and they are grouped around -33 e.u. Ethyl propionate and ethyl monochloroacetate have the same entropy value (-33 e.u.) although the enthalpy of adduct formation values differ by 4.0 kcal/mole. The ethyl trichloroacetate adduct has a $-\Delta H$ value of 3.05 kcal-mole⁻¹ and a $-\Delta S$ value of 15 e.u. which reflects the weak interaction in this adduct. The decrease in the ΔS values when going from ethyl propionate to ethyl pivalate (-34.7 e.u.) is probably due to additional steric contribution to the entropy from restriction in configurations of the alkyl groups which arises in the adducts.

In ethyl mono- and dichloroacetate there is a splitting of the carbonyl stretching frequency and spectra of the esters in solution contain two peaks.²⁰ The high frequency peak is associated with the more polar *cis* form in which

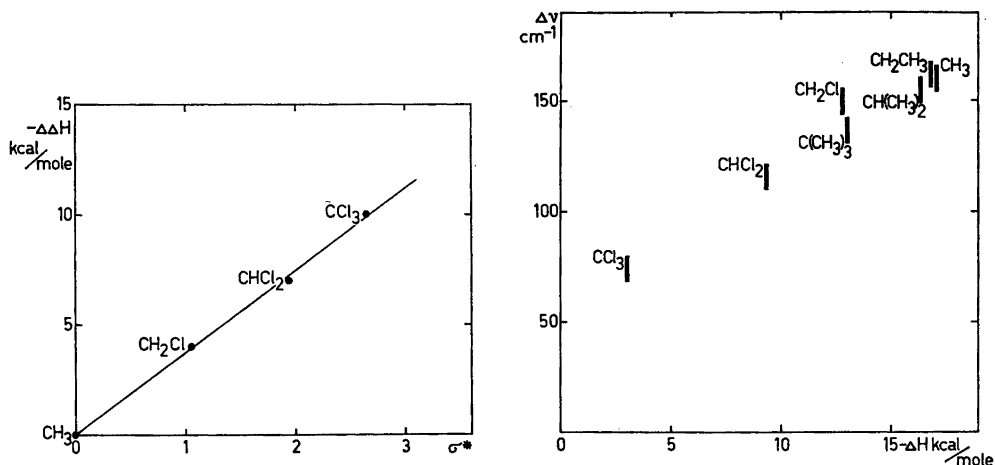


Fig. 1. Difference between enthalpies of adduct formation of methyl- and chloro-substituted ethyl acetates versus σ^* for the chloromethyl group.

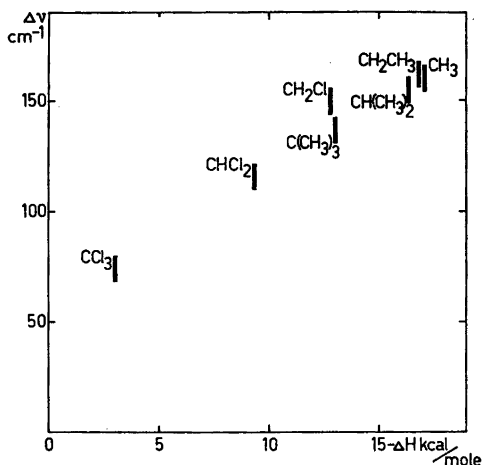


Fig. 2. Shift in carbonyl stretching frequency versus enthalpy of formation of adduct between SbCl_5 and RCOOC_2H_5 .

the oxygen and halogen atoms are close together. In ethylene chloride solution both forms exist although the *cis* form dominates. For ethyl dichloroacetate two distinct peaks, 17 cm^{-1} apart, appear but for ethyl monochloroacetate the carbonyl peak at 1749 cm^{-1} is asymmetric with a small shoulder at 1730–1735 cm^{-1} . It is assumed that the differences in frequency for *cis* and *gauche* forms are the same in both esters. The frequency for the *gauche* form of ethyl monochloroacetate then becomes 1732 cm^{-1} . In the adducts, the esters can be expected to be in the *gauche* form with the chlorine atoms as far as possible away from the carbonyl oxygen to avoid steric interaction with the chlorine atoms in antimony pentachloride. The shifts are therefore calculated from the low frequency peaks.

The shifts in carbonyl frequencies of the esters caused by adduct formation with antimony pentachloride show the same trend as with aluminium trichloride,³ tin tetrachloride,³ and titanium tetrachloride⁴ as acceptors. A closer comparison cannot be made as the solvents used are not the same and some of the measurements refer to solid adducts.

The shifts for the ethyl acetates follow the enthalpy changes, which is shown in Fig. 2. Thus, for as closely related donors as the substituted ethyl acetates the shifts in carbonyl frequency caused by adduct formation in solution can be used to estimate the relative donor strengths.

Added in proof: Dissociation constants of SbCl_5 adducts in ethylene chloride solution determined from spectroscopic experiments have recently been reported (Gutmann, V. and Mayer, U. *Monatsh. Chem.* **98** (1967) 294). For the SbCl_5 -ethyl acetate adduct the value 1.5×10^{-6} mole l^{-1} is reported, which differs by a factor of 43 from the value for the stability constant of the SbCl_5 -ethyl propionate adduct derived from calorimetric measurements. From the small difference between the ethylpropionate and ethyl iso-

butyrate adduct values it can be concluded that the stability constant of the ethyl acetate adduct should not differ much from that of ethyl propionate. The reason for the discrepancy between the results is obscure. Few details are given about the spectroscopic experiments but it is obvious that the evaluation of the water content in the solvent is of critical importance in this method.

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REFERENCES

1. Olofsson, G., Lindqvist, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 259.
2. Olofsson, G. *Acta Chem. Scand.* **18** (1964) 11.
3. Bystrov, D. S. *J. Strukt. Chem. USSR. (Eng. Transl.)* **4** (1963) 501.
4. Jain, S. C. and Rivest, R. *Can. J. Chem.* **40** (1962) 2243.
5. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 93.
6. Hollis, O. L. and Hayes, W. V. *J. Gas Chromatog.* **4** (1966) 235.
7. Sellers, P. *To be published.*
8. Wadsö, I. *Sci. Tools* **13** (1966) 33.
9. Cameron, A. E. and Wichers, E. *J. Am. Chem. Soc.* **84** (1962) 4175.
10. Bolles, T. F. and Drago, R. S. *J. Am. Chem. Soc.* **87** (1965) 5015.
11. Nelander, B. *Acta Chem. Scand.* **20** (1966) 2289.
12. Månsson, M., Sellers, P. and Sunner, S. *To be published.*
13. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 1887.
14. O'Gorman, J. M., Shand, W., Jr. and Schomaker, V. *J. Am. Chem. Soc.* **72** (1950) 4222.
15. Brun, L. *Acta Cryst.* **20** (1966) 739.
16. Rosado-Lojo, O., Hancock, C. K. and Danti, A. *J. Org. Chem.* **31** (1966) 1899.
17. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press 1960, p. 260.
18. Taft, R. W., Jr. In Newman, M. S. *Steric Effects in Organic Chemistry*, Wiley, New York 1956, p. 619.
19. Person, W. B. *J. Am. Chem. Soc.* **84** (1962) 536.
20. Brown, T. L. *J. Am. Chem. Soc.* **80** (1958) 3513.

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