

Thermodynamic Properties and Frequency Shifts of Some Molecular Adducts of Antimony Pentachloride and Molecules Containing the Carbonyl Group

GERD OLOFSSON

Thermochemistry Laboratory, University of Lund, Lund, Sweden*

Enthalpies and entropies of formation for some antimony pentachloride adducts of molecules containing the carbonyl group are discussed in terms of the inductive, resonance, and steric effects of the groups attached to the carbonyl group. The use of the carbonyl stretching frequency shifts between free and bound donors as a measure of strength of donor-acceptor interaction is examined. Finally, a comparison is made between the first ionization potentials of some donors and their enthalpies of adduct formation.

This paper summarizes and discusses reaction calorimetric and infrared spectroscopic measurements on adduct formation reactions between antimony pentachloride and organic molecules containing the carbonyl group which the author performed during the years 1961—1967.^{1-10,**} In these adducts the carbonyl oxygen acts as the electron donating atom. The change in the immediate environment of the donor-acceptor bond for various donors should be small as the different substituents are attached to the atom next to the bonding atom. Thermodynamic data (ΔH , ΔG , and ΔS) for the formation of these adducts should reflect the inductive influence of various substituents in the donor molecules as well as non-bonding interactions between donor and acceptor.

The carbonyl stretching frequency appears at a markedly lower frequency in the adduct than in the free donor molecule. This has been used to confirm

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** A general treatment of molecular adducts of oxo-compounds can be found in the monograph by Lindqvist.¹¹ It contains a compilation of known molecular adducts of that type, a review of different methods of investigation and a theoretical treatment of the donor-acceptor interaction. The coordination chemistry of antimony pentachloride has been treated in a review concerning addition compounds of group V pentahalides.¹² It covers the literature up to December 1964.

the formation of donor-acceptor adducts between Lewis acids and various donors (*cf.*, *e.g.*, Refs. 13, 14, 15 and references therein). It has been claimed that the shift in carbonyl frequency could be used as a measure of the strength of donor-acceptor interaction.¹⁶ There is, however, a lack of systematic inves-

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

Donor	$-\Delta H$ kcal.mole ⁻¹	Donor	$-\Delta H$ kcal.mole ⁻¹
Me_2CO^1	17.03 ± 0.04	$\text{MeO}(\text{Me})\text{CO}^1$	16.38 ± 0.03
$\text{Me}(\text{Et})\text{CO}^2$	17.43 ± 0.03	$\text{MeO}(\text{Et})\text{CO}^2$	16.23 ± 0.01
$\text{Me}(\text{Pr})\text{CO}^3$	17.50 ± 0.02	$\text{EtO}(\text{H})\text{CO}^3$	17.00 ± 0.07
$\text{Me}(i\text{-Pr})\text{CO}^2$	17.07 ± 0.03	$\text{EtO}(\text{Me})\text{CO}^1$	17.08 ± 0.05
$\text{Me}(t\text{-Bu})\text{CO}^2$	16.95 ± 0.03	$\text{EtO}(\text{Pr})\text{CO}^1$	16.76 ± 0.05
Et_2CO^4	16.53 ± 0.03	$i\text{-PrO}(\text{Me})\text{CO}^1$	17.53 ± 0.05
$\text{Et}(i\text{-Pr})\text{CO}^4$	16.16 ± 0.03	$i\text{-PrO}(t\text{-Bu})\text{CO}^5$	13.5 ± 0.3
$\text{Et}(t\text{-Bu})\text{CO}^4$	14.58 ± 0.01		
$i\text{-Pr}_2\text{CO}^4$	16.20 ± 0.03	$(\text{MeO})_2\text{CO}^1$	15.17 ± 0.03
$i\text{-Bu}_2\text{CO}^5$	16.38 ± 0.02	$(\text{EtO})_2\text{CO}^1$	15.98 ± 0.05
$\text{neoPe}_2\text{CO}^6$	15.00 ± 0.10	$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}^6$	17.49 ± 0.01
$\text{CH}_3-(\text{CH}_2)_4-\text{CO}^6$	17.79 ± 0.01	 O	
$\text{Me}_2\text{N}(\text{Me})\text{CO}^3$	27.80 ± 0.08		
$(\text{Me}_2\text{N})_2\text{CO}^3$	29.64 ± 0.03		
$\text{Me}_2\text{N}(\text{EtO})\text{CO}^5$	22.37 ± 0.03		
$\text{Me}_2\text{N}(\text{CF}_3)\text{CO}^5$	16.58 ± 0.02		
$\text{Me}_2\text{N}(\text{Cl})\text{CO}^5$	17.22 ± 0.01		

Table 2. Thermodynamic quantities for the formation of adducts between SbCl_5 and various donors in ethylene chloride solution.

Donor	$-\Delta H$ kcal.mole ⁻¹	K l.mole ⁻¹	$-\Delta G^a$ kcal.mole ⁻¹	$-\Delta S$ e.u.
$t\text{-Bu}(i\text{-Pr})\text{CO}^6$	11.60 ± 0.03	$(3.7 \pm 0.3)10^8$	2.97 ± 0.05	28.9 ± 0.2
$t\text{-Bu}_2\text{CO}^{6b}$	9.6 ± 0.1	$(3.3 \pm 0.8)10^8$	1.54 ± 0.13	27.0 ± 0.4
	0.3	(0.3)	0.05	1.1
$t\text{-Bu}(\text{neoPe})\text{CO}^6$	11.78 ± 0.10	$(2.65 \pm 0.35)10^8$	1.41 ± 0.08	34.8 ± 0.4
$\text{MeO}(\text{CF}_3)\text{CO}^6$	2.7 ± 0.4	$(6.1 \pm 1.0)10^{-1}$	-2.2 ± 0.1	16.4 ± 1.4
$\text{MeO}(t\text{-Bu})\text{CO}^6$	12.83 ± 0.06	$(7.8 \pm 0.8)10^8$	2.05 ± 0.06	36.2 ± 0.3
$\text{EtO}(\text{Et})\text{CO}^7$	16.82 ± 0.01	$(3.0 \pm 0.7)10^8$	6.94 ± 0.15	33.1 ± 0.5
$\text{EtO}(i\text{-Pr})\text{CO}^7$	16.37 ± 0.02	$(8.8 \pm 2.6)10^8$	6.21 ± 0.20	34.1 ± 0.6
$\text{EtO}(t\text{-Bu})\text{CO}^7$	13.03 ± 0.04	$(2.3 \pm 0.1)10^8$	2.69 ± 0.04	34.7 ± 0.2
$\text{EtO}(\text{CH}_2\text{Cl})\text{CO}^7$	12.80 ± 0.01	$(3.8 \pm 0.5)10^8$	2.98 ± 0.07	32.9 ± 0.2
$\text{EtO}(\text{CHCl}_2)\text{CO}^7$	9.35 ± 0.05	$(4.9 \pm 0.2)10^1$	0.41 ± 0.03	30.0 ± 0.2
$\text{EtO}(\text{CCl}_2)\text{CO}^7$	3.05 ± 0.07	$(1.7 \pm 0.2)10^0$	-1.60 ± 0.06	15.6 ± 0.3
$\text{Et}(\text{Cl})\text{CO}^6$	3.3 ± 0.2	$(1.4 \pm 0.1)10^1$	-0.33 ± 0.04	12.0 ± 1.0

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

^b Not corrected for the statistical factor 2. The corrected values are: $-\Delta G = 1.13$ kcal.mole⁻¹ and $-\Delta S = 28.5$ e.u.

Table 3. Infrared spectra measurements performed on ethylene chloride solutions of free donors and of SbCl_5 adducts.

Donor	Carbonyl stretching frequency cm^{-1}		shift cm^{-1}
	free donor	adduct	
Et_2CO^a	1702	1590	112 ± 5
$\text{CH}_2-(\text{CH}_2)_4-\text{CO}^b$	1698	1592	106 ± 5
t-Bu(i-Pr)CO^a	1690	1608	82 ± 7
$\text{t-Bu}_3\text{CO}^a$	1670	1630	40 ± 7
$\text{neoPe}_3\text{CO}^a$	1693	1573	120 ± 7
$\text{MeO}(\text{CF}_3)\text{CO}^b$	1782	1728	54 ± 8
$\text{MeO}(\text{Me})\text{CO}^a$	1735	1580	155 ± 7
$\text{EtO}(\text{Me})\text{CO}^c$	1725	1565	160 ± 6
$\text{EtO}(\text{Et})\text{CO}^c$	1722	1560	162 ± 7
$\text{EtO}(\text{i-Pr})\text{CO}^c$	1720	1565	155 ± 7
$\text{EtO}(\text{t-Bu})\text{CO}^c$	1712	1575	137 ± 7
$\text{EtO}(\text{CH}_2\text{Cl})\text{CO}^c$	1749	1582	150 ± 7
	1732		
$\text{EtO}(\text{CHCl}_2)\text{CO}^c$	1755	1622	116 ± 7
	1738		
$\text{EtO}(\text{Cl}_2)\text{CO}^c$	1757	1683	74 ± 7
$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}^b$	1766	1615	151 ± 6
O			
$\text{Et}(\text{Cl})\text{CO}^d$	1782	1585	197 ± 6

^a Unpublished results.

tigations of frequency shifts and enthalpies (or free energies) of adduct formation of various donors with a reference acceptor.

Summaries of the experimental results¹⁻⁹ are given in Tables 1-3. The reaction mixtures in the calorimetric and spectroscopic experiments were ethylene chloride solutions 0.01-0.03 M in donor and usually about 0.05 M in SbCl_5 . In cases where conversion to adduct was not complete in the concentration region used, it was possible to determine from reaction calorimetric experiments both the enthalpy of formation and the stability constant, K , for the adduct.⁷ For very strong adducts a direct determination of K was not possible. Instead, the equilibrium constant was determined for a substitution reaction.⁷ The thermodynamic quantities refer to the adduct formation reaction with both reactants and reaction product in ethylene chloride solution at 25°C. The ΔG values have been calculated from K values expressed in atm^{-1} .

$$K_p(\text{atm}^{-1}) \cdot 24.46 (\text{l} \cdot \text{atm} \cdot \text{mole}^{-1}) = K_c (\text{l} \cdot \text{mole}^{-1})$$

As a rule, enthalpies of adduct formation referring to gas phase reactions cannot be determined since it is not possible to measure heats of vaporization of the adducts. It must therefore be assumed that enthalpies of formation of adducts in an inert solvent closely parallel the enthalpies of formation in the gas phase. It is also assumed that differences in the enthalpy of formation values represent differences in the potential energy of the adducts and thus

that differences in energies of molecular motion between adducts of various donors are of minor importance (*cf.* Ref. 17). In the following discussion the enthalpy of adduct formation is used as a measure of the strength of donor-acceptor interaction.

Considering the arrangement around the carbonyl oxygen in, *e.g.*, the addition compounds $\text{Br}_2\text{-Me}_2\text{CO}$ ¹⁸ and $\text{SbCl}_5\text{-HCONMe}_2$,¹⁹ whose structures have been determined in the solid state, it seems reasonable to assume sp^2 hybridization of the oxygen atom. The carbonyl group in a compound of formula R_iXCOYR_j * can then be described as a carbon atom with sp^2 hybridized orbitals which forms one σ - and one π -bond to an oxygen atom. The remaining lone-pair electrons of the oxygen atom lie in the same plane as the X-CO-Y moiety. If the groups attached to the carbonyl group are identical the two electron pairs are equivalent but if the groups differ the electron pairs are in different environments. Then the acceptor molecule has, in principle, two different sites to choose between for coordination. In the solid adduct $\text{SbCl}_5\text{-HCONMe}_2$ the angle $\text{C}=\hat{\text{O}}\text{-Sb}$ is 124.5° and bonding is to the electron pair at the same side as the hydrogen atom. In solid $[\text{TiCl}_4\text{-MeCOOEt}]_2$ ²⁰ the Ti atom coordinates at the lone electron pair on the carbonyl oxygen, which is on the same side as the methyl group. The alkoxy group is in a position *cis* to the carbonyl group in the adduct, as in the free ester. It seems reasonable to assume that simple esters in adducts in solution also have the *cis* configuration. In ketone adducts the acceptor will coordinate at the site which gives a minimum of steric hindrance (*cf.* Ref. 21). The stability constants for adducts of symmetrical donor molecules may need to be corrected for the statistical factor 2 to account for the two identical sites and make them comparable with the stability constants of asymmetrical donors (see, *e.g.*, Ref. 22).

EFFECTS OF VARIOUS ATOMS ATTACHED TO THE CARBONYL GROUP

Representative values of enthalpies of formation of $\text{SbCl}_5\text{-XCOY-}$ adducts are shown in Table 4. It is seen that in addition to the inductive effect of the groups, reflecting the electronegativity of the X and Y atoms ($\text{C} < \text{N} \sim \text{Cl} < \text{O}$),²³ a positive resonance effect of the dialkylamino and alkoxy groups is revealed by the enthalpy values.

Substitution of a dimethylamino group for a methyl group in acetone to give dimethylacetamide leads to an increase in the $-\Delta H$ value of $11 \text{ kcal}\cdot\text{mole}^{-1}$. Conjugation of the lone-pair electrons at the nitrogen atom with the π -bond in the carbonyl group is considered to be the reason for the increased donor ability of the oxygen atom in the amide.¹¹

The enthalpies of adduct formation of an alkyl carboxylate and a ketone are found to be of the same magnitude. If comparisons are made between ketones and corresponding esters where an ether oxygen has been substituted for a methylene group of the ketone the esters give at the most $1 \text{ kcal}\cdot\text{mole}^{-1}$ lower $-\Delta H$ values than the corresponding ketones. The difference between

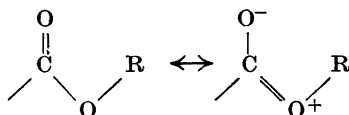
* R_i and R_j represent alkyl groups, H, Cl, and F atoms and combinations thereof; $i, j = 0, 1, 2$ or 3 . The atoms X and Y are any two of the elements carbon, nitrogen, oxygen and chlorine.

Table 4. Enthalpy of formation values of $\text{SbCl}_5 \cdot \text{XCOY}$ adducts.

Y \ X	C	N	O	Cl
C	17	28	16	3
N		30	22	17
O			15	^a
Cl				^b

^a Could not be determined.⁶^b Not measured.

the $-\Delta H$ values of MeCOEt and MeCOOMe is 1.1, between Et_2CO and EtCOOMe 0.3, and between MeCOPr and MeCOOEt 0.4 $\text{kcal}\cdot\text{mole}^{-1}$. Obviously, the alkoxy groups exert a positive resonance effect which almost balances the $-I$ effect.¹¹



Propionyl chloride gave a $-\Delta H$ value 14 $\text{kcal}\cdot\text{mole}^{-1}$ lower than methyl ethyl ketone. Me_2NCOCl and $\text{Me}_2\text{NCOCF}_3$ were found to give approximately the same enthalpy of adduct formation values, about 11 $\text{kcal}\cdot\text{mole}^{-1}$ lower than the value for Me_2NCOMe . As the inductive effect of the chlorine atom and the trifluoromethyl group is of the same magnitude, σ_I values 0.47 and 0.41,²⁴ respectively, it can be concluded that if there is any positive resonance

effect of the chlorine atom (a conjugation of the type $-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \leftrightarrow -\overset{\text{O}^-}{\parallel}{\text{C}}=\text{Cl}^+$) it should be small.

The substitution of an ethoxy group for the methyl group in Me_2NCOMe to give Me_2NCOOEt leads to a decrease in the $-\Delta H$ value of 5 $\text{kcal}\cdot\text{mole}^{-1}$. If $-\Delta H$ values of Me_2NCOZ adducts are plotted against the σ_I values of Z a fairly good linear relation is found (Fig. 1). It seems that the ethoxy group does not exert any positive resonance effect in ethyldimethyl carbamate.

The $-\Delta H$ value for $(\text{Me}_2\text{N})_2\text{CO}$ is 2 $\text{kcal}\cdot\text{mole}^{-1}$ higher than the value for Me_2NCOMe . Also, for the second dimethylamino group the resonance effect exceeds the negative inductive effect ($\sigma_I = +0.10$)²⁴ although to a less extent than for the first one.

The difference in enthalpies of adduct formation between a monoester and an alkyl carbonate is of the order of 1 $\text{kcal}\cdot\text{mole}^{-1}$, the same as the difference found between ΔH values of a ketone and an ester. Thus the balance of the

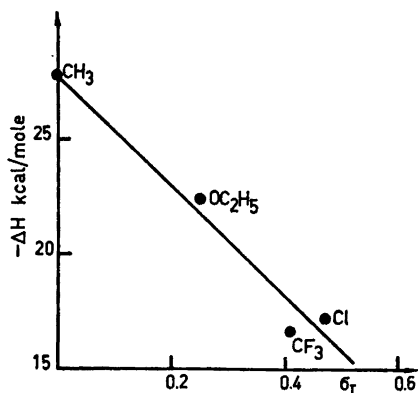


Fig. 1. Plot of enthalpy of formation of $(\text{CH}_3)_2\text{NCOZ}$ adduct against σ_I of Z. $\sigma_I(\text{EtO})$ assumed to be the same as $\sigma_I(\text{MeO})$ (Ref. 24).

inductive and resonance effects of the alkoxy group found in the monoester is also revealed in the alkyl carbonates.* The inductive effect alone could be expected to cause a decrease in the $-\Delta H$ value of at least $5 \text{ kcal}\cdot\text{mole}^{-1}$ (cf. Me_2NCOOEt and Me_2NCOMe). Esters seem to be slightly more susceptible to inductive effects than amides, the difference in the $-\Delta H$ values of MeCOOMe and CF_3COOMe being $14 \text{ kcal}\cdot\text{mole}^{-1}$ while the difference is $11 \text{ kcal}\cdot\text{mole}^{-1}$ between Me_2NCOMe and $\text{Me}_2\text{NCOCF}_3$.

From a recent determination of enthalpies of combustion of ethyl propionate and diethyl carbonate the stabilization energy is calculated to be $19 \text{ kcal}\cdot\text{mole}^{-1}$ in the ester and 27 or $31 \text{ kcal}\cdot\text{mole}^{-1}$, depending on the choice of reference substance, in the carbonate²⁵ (cf. Ref. 26, p. 86 ff). Provided that the inductive effect is unaltered it seems as if there is a difference in conjugation of the alkoxy groups between free and bound alkyl carbonate, since the enthalpy of adduct formation values indicate cancellation of the inductive and resonance effects in both monoesters and alkyl carbonates.

EFFECTS OF ALKYL SUBSTITUENTS

The $-\Delta H$ values for adduct formation, with SbCl_5 as acceptor, have been shown to increase through the following series of donors:



The increase in $-\Delta H$ with increasing alkyl substitution is in accordance with chemical evidence expressed as +I effect of the alkyl groups.²⁷ It may

* It is clear that the steric effects which are difficult to take into account make it impossible to differentiate between the degree of inductive and resonance effects that the alkoxy group exerts in a monoester and in an alkyl carbonate as has been attempted in Ref. 1 and Ref. 11, p. 103.

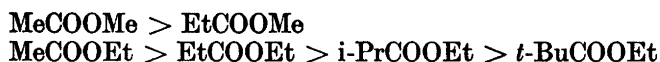
** MeCOOi-Bu could not be determined.²

be noticed that, in each series of donors, the environment of one of the electron pairs on the carbonyl oxygen atom is unchanged.

Conversely, the $-\Delta H$ value of Et_2CO was found to be $0.9 \text{ kcal}\cdot\text{mole}^{-1}$ lower than the value for MeCOEt and the difference between MeCOi-Pr and EtCOi-Pr is similar. In these cases methyl groups are substituted for α -hydrogen atoms also in the remaining methyl group. It seems that the decrease in the $-\Delta H$ values could be due to non-bonding interactions between donor and acceptor molecules, although model studies suggest that the adducts should be formed without strain. This assumption is strengthened by the fact that the $-\Delta H$ value for cyclohexanone is $1.3 \text{ kcal}\cdot\text{mole}^{-1}$ higher than the value for Et_2CO . The alkyl groups in the cyclic ketone are held back in a rigid position and the carbonyl group can coordinate with the acceptor with a minimum of steric interaction. In straight-chain ketones, the alkyl group (other than methyl) close to the acceptor may to some extent have lost its rotational freedom around the carbonyl- α -carbon bond.

It is probable that a direct non-bonding repulsion interaction starts to become significant in the $\text{EtCO}t\text{-Bu}$ adduct. The internal strain in the adduct becomes more pronounced when the bulkiness of the donor molecules increases to the size of $i\text{-PrCO}t\text{-Bu}$ or $t\text{-Bu}_2\text{CO}$. The results obtained for $i\text{-Bu}_2\text{CO}$ and neoPe_2CO show that the enthalpy of adduct formation is much less sensitive to methyl substitution in the β -position than in a position α - to the carbonyl group. The effects of the alkyl groups on the enthalpies of adduct formation of the symmetrical ketones do not show any correlation with Taft's E_s values.²⁸

Substitution of methyl groups for α -hydrogen atoms in alkyl carboxylates leads to an observed decrease in the $-\Delta H$ values:



For the mono- and disubstituted acetates there is still one α -hydrogen atom left which may occupy the position *cis* to the carbonyl bond and an adduct could probably form which is free from direct steric interactions between the acceptor molecule and the substituents. In α,α,α -trisubstituted acetates, model studies suggest direct steric interaction between the ester molecule and the chlorine atoms in antimony pentachloride irrespective of which lone-pair is preferred for coordination.

The adduct formation of γ -butyrolactone was found to be $0.6 \text{ kcal}\cdot\text{mole}^{-1}$ more exothermic than that of EtCOOEt . In the cyclic ester the alkoxy group is in a position *trans* to the carbonyl bond and tied to the alkyl group. The reduced steric interaction in this adduct seems to be the reason for its higher $-\Delta H$ value, although the difference may hardly be significant.

EFFECTS OF ELECTRONEGATIVE SUBSTITUENTS

When chlorine atoms are substituted for α -hydrogen atoms in ethyl acetate, to give ethyl mono-, di-, and trichloroacetate, the steric effect of the chlorine atoms on the enthalpy of adduct formation can be accounted for by comparison

with the corresponding methyl-substituted esters, the chlorine atom and the methyl group having van der Waals radii of 1.8 ± 0.1 and 2.0 ± 0.1 Å,²³ respectively. 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 chlorine-substituted as for methyl-substituted ethyl acetates.⁷ The possible inductive effect of the methyl group is in any case small and may be neglected in comparison with the effect of the chlorine atom. If the differences between the enthalpies of adduct formation of the methyl-substituted and corresponding chlorine-substituted esters are plotted against Taft's σ^* values of the chloromethyl groups²⁸ a good linear relation is obtained (Fig. 2).

ENTROPY OF ADDUCT FORMATION

In many cases a linear relation exists between entropy and enthalpy of formation of donor-acceptor complexes of a reference acceptor with a series of related donors (see, *e.g.*, Ref. 17 and references therein). A linear ΔS — ΔH relation has also been reported for adducts of SnCl_4 with five donors of different kinds.²⁹ *

A plot of ΔS versus ΔH values found in the present investigation is shown in Fig. 3. Although the expected trend is found (*cf.* Ref. 17) the data cannot be linearly represented and this for obvious reasons: the steric requirements of the donors are very different. That this factor is not the only reason for the

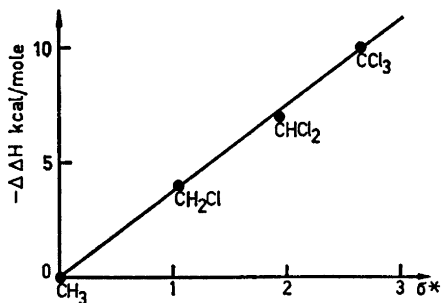


Fig. 2. Difference between enthalpies of adduct formation of methyl- and chloro-substituted ethyl acetates versus σ^* for the chloromethyl group.

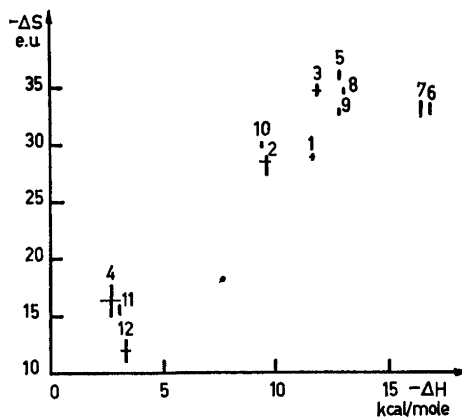


Fig. 3. Entropy versus enthalpy of adduct formation. 1. *t*-Bu(*i*-Pr)CO. 2. *t*-Bu₂CO (corrected value). 3. *t*-Bu(neoPe)CO. 4. MeO(CF₃)CO. 5. MeO(*t*-Bu)CO. 6. EtO(Et)CO. 7. EtO(*i*-Pr)CO. 8. EtO(*t*-Bu)CO. 9. EtO(CH₂Cl)CO. 10. EtO(CHCl₂)CO. 11. EtO(CCl₃)CO. 12. Et(Cl)CO.

* 12.8 e.u. should be added to the $-\Delta S$ values reported in Ref. 29 as the conversion from K in units $\text{l}\cdot\text{mole}^{-1}$ to K in atm^{-1} is wrong by a factor of 24.9^2 ($\text{l}^2\cdot\text{atm}^2\cdot\text{mole}^{-2}$).

lack of a linear $\Delta S - \Delta H$ relation is shown by the comparison between EtCOOEt and CH₂ClCOOEt which show the same entropy values while the ΔH values differ by 4 kcal·mole⁻¹.

The difference of 6 e.u. between the *tert*-butyl isopropyl ketone and *tert*-butyl neopentyl ketone adducts, ΔH equal, probably reflects that the alkyl groups of the donors become more interlocked upon adduct formation in the second ketone than in the first. The slight increase in the $-\Delta S$ values in the series ethyl mono-, di-, and trimethylacetate is probably due to the increase in the size of the alkyl group.

In view of the results presented in Fig. 3 it is a little surprising that a linear $\Delta S - \Delta H$ relation was found in Ref. 29 as the donors studied are expected to exert pronounced differences in steric interaction in the adducts.

CARBONYL FREQUENCY SHIFTS

Relative shifts of the carbonyl stretching frequency for a reference donor in adducts with different Lewis acids have been ascribed to differences in strength of donor-acceptor interaction (see, *e.g.*, Ref. 30 and references therein and Ref. 31). It has been questioned, however, if it is meaningful to make such comparisons.^{32,33} In the present investigation of shifts in carbonyl frequency between free donor and donor bound to SbCl₅ the adducts are more closely related as the donor-acceptor bond is formed by the same atoms than adducts between varying acceptors and a reference donor.

In discussions of relative frequency shifts the fact that the frequency of the C=O group in the bound donor may be influenced by variations in the

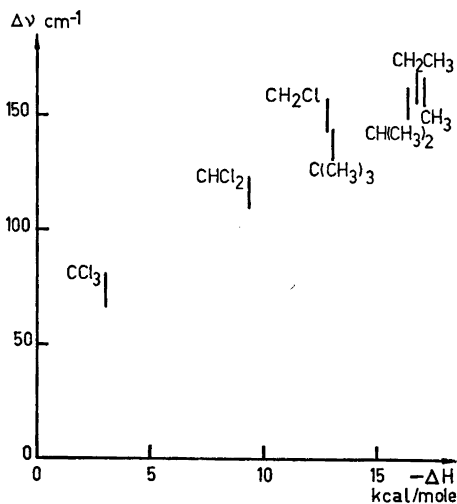


Fig. 4. Shift in carbonyl stretching frequency versus enthalpy of formation of adduct between SbCl₅ and RCOOEt.

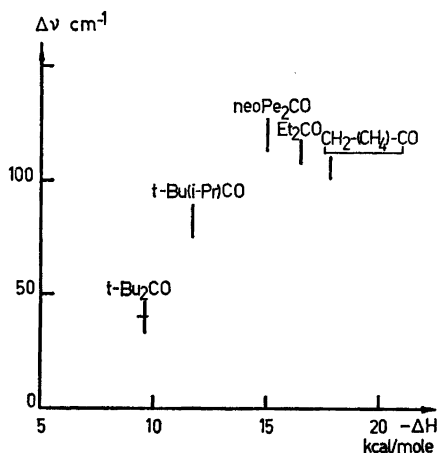


Fig. 5. Shift in carbonyl frequency versus enthalpy of adduct formation for various ketones.

structure of the adduct has usually been neglected. It is reasonable to assume that the $\nu_{C=O}$ depends, *i.a.*, on the bond angle $C=\hat{O}\cdot\cdot A$ (A is the central atom in the acceptor molecule). It is known from structural data that this bond angle differs, *e.g.* in $SbCl_5 \cdot HCONMe_2$ ¹⁹ the $C=\hat{O}\cdot\cdot Sb$ angle is 124.5° while it is 149° in $SbCl_5 \cdot PhCOCl$.^{34,35} In $(TiCl_4 \cdot MeCOOEt)_2$ ²⁰ the $C=\hat{O}\cdot\cdot Ti$ angle is 152.1° .

For a series of adducts between $SbCl_5$ and esters of the formula $RCOOEt$ there is a fairly good correlation between $\Delta\nu_{C=O}$ and $-\Delta H$ for the adduct formation (Fig. 4). Apparently, the adducts of the substituted ethyl acetates are closely enough related to allow conclusions regarding donor strength to be drawn from frequency shifts. On the other hand the difference in the $-\Delta H$ values of $EtCOOEt$ and Et_2CO is $0.3 \text{ kcal}\cdot\text{mole}^{-1}$ while the difference in carbonyl frequency shifts is 50 cm^{-1} , the ketone showing the smaller shift. Propionyl chloride was found to be a weak donor but still the shift in carbonyl frequency was found to be 197 cm^{-1} , that is 35 cm^{-1} larger than the shift with ethyl propionate. It seems that at least in the case studied constancy in the atoms attached to the carbonyl group is a prerequisite for a satisfactory linear correlation between $\Delta\nu_{C=O}$ and $-\Delta H$. Constant next-neighbour atoms are, however, not a sufficient condition for a linear relation as can be seen in Fig. 5 where $\Delta\nu_{C=O}$ is plotted against $-\Delta H$ for adduct formation of five ketones. The steric requirements differ widely in this series of donors.

Table 5. First ionization potentials of some molecules containing the carbonyl group.

Compound	Ionization potential eV (Error limits $\leq 0.03 \text{ eV}$)
Me_2CO	9.71 ^{a,b}
$Me(Et)CO$	9.54 ^{a,b}
$Me(Pr)CO$	{ 9.47 ^a 9.39 ^b
$Me(i-Pr)CO$	9.32 ^b
$Me(t-Bu)CO$	9.18 ^{a,b}
Et_2CO	9.34 ^{a,b}
$Et(t-Bu)CO$	8.98 ^a
$i-Pr(t-Bu)CO$	8.82 ^a
$t-Bu_2CO$	8.65 ^a
$i-Bu_2CO$	9.04 ^a
$CH_2-(CH_2)_4-CO$	9.14 ^{a,b}
$MeO(Me)CO$	10.27
$MeO(Et)CO$	10.15 ^b
$EtO(H)CO$	10.61 ^b
$EtO(Me)CO$	10.09 ^{a,b}
$EtO(Et)CO$	10.00 ^b
$EtO(CH_2Cl)CO$	10.20 ^a
$EtO(CCl_3)CO$	10.44 ^a
$i-PrO(Me)CO$	9.99 ^b
$Me_2N(Me)CO$	8.81 ^b

^a Ref. 36.

^b Ref. 37.

IONIZATION POTENTIALS OF THE DONOR MOLECULES

For molecules containing the carbonyl group it has been assumed that the first ionization refers to the removal of one of the oxygen lone-pair electrons.^{36,37} For a number of compounds values of the first ionization potential obtained by the photoionization method have been collected in Table 5.

It has been suggested that the donor strength of a molecule should depend largely on the ionization potential and the approachability of the donor.³⁸ It does not seem likely that the approachability of an ester molecule and a ketone should differ significantly. The enthalpies of adduct formation of an alkyl alkanoate and a ketone with antimony pentachloride as acceptor are of the same magnitude. However, the ionization potential values differ by about 0.5 eV, the ester having the higher value.

Ethyl acetate and ethyl formate show the same $-\Delta H$ values while the I_p values differ by 0.5 eV. Pronounced differences in steric interactions between the adducts are unlikely as the esters only differ in groups attached to the atom next to the bonding atom.

The influence on the ionization potentials of substitution of methyl groups for α -hydrogen atoms in acetone gives a decrease of 0.18 eV per methyl group while chlorosubstitution gives an increase of 0.20 eV per chlorine atom.³⁶ Substitution of chlorine for hydrogen atoms in a position α - to the carbonyl group in methyl and ethyl acetates gives an even smaller increase in the I_p values, about 0.10–0.12 eV per chlorine atom.³⁶ On the other hand, the $-\Delta H$ value for ethyl monochloroacetate is 4.3 kcal·mole⁻¹ lower than the value for ethyl acetate while methyl ethyl ketone gives a $-\Delta H$ value 0.4 kcal·mole⁻¹ higher than acetone.

In these cases there is no correlation between the I_p and $-\Delta H$ values. One explanation could be that the first ionization potentials at least in some cases do not refer to the lone-pair electrons (*cf.* Ref. 39).

CONCLUSIONS

The experimental results show that the enthalpy of adduct formation is influenced by the inductive and resonance effects in the donor molecule as well as by steric interactions between donor and acceptor. In the absence of resonance effects the $-\Delta H$ values give a linear correlation with the inductive constants of the substituents provided that the steric effects are accounted for.

The ΔH and ΔS values in the present investigation appear not to show any linear enthalpy–entropy relation. This partly could be due to differences in steric requirements of the donor molecules.

A linear correlation between ΔH and $\Delta\nu_{C=O}$ values seems not to exist unless the donor molecules show profound structural similarities.

The first ionization potentials of the donors do not correlate with the enthalpy of adduct formation values found in this study.

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