ACTA CHEMICA SCANDINAVICA 18 (1964) 11–17

Heats of Formation of Adducts between Antimony Pentachloride and some Ketones and Carboxylic Esters

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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 was the acceptor and the following carbonyl compounds were donors; the obtained heat of formation values in kcal.mole^{-1} are given within brackets: methyl ethyl ketone (17.43), methyl isopropyl ketone (17.07), pinacolin (16.95), ethyl propionate (16.82), ethyl isobutyrate (16.44), ethyl pivalate (12.93). *t*-Butyl acetate gives a much higher heat of reaction value, 36.0 kcal.mole^{-1}, which, together with the fact that the process was not instantaneous, strongly indicated that a chemical reaction took place. The obtained data have been discussed.

The formation of electron donor-acceptor adducts gives many opportunities of studying the influence of nearest neighbour effects by varying the substituents in the donating and/or accepting molecules. In most cases so far studied, the substituents have been directly attached to the donating or accepting atom or to both. Thus, in H. C. Brown's classical work on the thermodynamic properties of adducts with boron as acceptor and nitrogen as donor atoms, the influence of alkyl groups was thoroughly investigated.[1]

During recent years compounds of the general type $R_1 \cdots R_i X-O$ have aroused a particular interest as donor molecules.** The oxygen atom acts as immediate donor and the presence of the X—O group increases the experimental possibilities of studying the donor-acceptor bond properties. At the same time, the immediate environment of the donor-acceptor bond is only slightly, if at all, changed by a variation in the R's and non-bonded interactions between them and the acceptor molecule are less pronounced in comparison to cases in which the substituents are directly attached to the donating atom.

* Sponsored by the *Swedish Natural Science Research Council* and the *Swedish Technical Research Council.*

** For an extensive systematic treatment see the recent monograph by I. Lindqvist.[2] This author has covered the literature up to the beginning of 1962.

A few investigators have been particularly concerned with the elucidation of next neighbour effects by varying R. Osipov *et al.* have studied the dependence of heats of adduct formation on the size of alkyl radicals in aliphatic esters, where X = carbon and i = 2; R_1 is an alkyl and R_2 an ethoxy group.[3-4] A systematic study of adducts using oxo-compounds as donors was initiated by Lindqvist *et al.*[2] In the course of this work a qualitative calorimetric investigation was undertaken on the relative donor strength of a number of molecules with X equal to As, C, P, S, and Se, and R equal to Alk, Ar, AlkO, ArO, Me_2N, and H (dimethylformamide).[2,5-7] Later, quantitative measurements were done on the heats of formation in 1,2-dichloroethane solution of adducts between $SbCl_5$ and acetone, four alkylcarboxylates and two alkylcarbonates.[8]

The present investigation is a direct continuation of this work. It represents part of a study on the effects of a systematic variation in R in compounds of the general formula $R_1R_2C{=}O$. R_1 and R_2 will be attached to the carbonyl group through either two of the elements carbon, nitrogen, oxygen, or chlorine. This paper, together with the previous one,[8] covers cases in which carbon and oxygen are nearest neighbours.

EXPERIMENTAL*

Materials

The purification of all chemicals was done by fractional distillation (see Ref.[8]) and the progress was followed by GLC, using dioctylphthalate on Celite as stationary phase (where not otherwise stated). Except for isobutyrate, all chemicals used were found to be of a purity equal to or better than 99.8 %. The purity of the esters was also checked by titration after alkaline hydrolysis. Boiling points are given at 760 mm Hg, refractive indices for the D-line at 25°.

Ethylene chloride and antimony pentachloride were treated as given in Ref.[8]

Methyl ethyl ketone (Kebo), *methyl isopropyl ketone* (BDH) and *t-butyl ketone* (*pinacolin*, Fluka) showed b.p.'s and refractive indices of 79.8° and 1.3765; 94.5° and 1.3857; 106.4° and 1.3948, respectively.

Ethyl propionate (Kebo) b.p. 99.1°, n 1.3820. Hydrolysis gave a purity of 99.8 ± 0.1 %.

Two commercial samples of *ethyl isobutyrate* (Schuckardt and Fluka) were found to be identical and contained a contaminant that was not possible to remove by straightforward distillation. By using GLC and two different stationary phases (dioctylphthalate on Celite and polyethyleneglycol on teflon) it was shown that *ca.* 5 % of toluene was present after a first distillation – other impurities had been removed. Most of the toluene was removed by repeated distillation after addition of ethanol (no distinct ternary azeotrope was formed). The final sample contained 0.8 ± 0.2 % toluene as judged from GLC. Alkaline hydrolysis indicated a purity of 98.7 ± 0.3 %. B.p. 110.6, n 1.3867.

Ethyl pivalate (Fluka) b.p. 118.5, n 1.3885. Purity as judged from hydrolysis [9] 99.8 ± 0.2 %.

t-Butyl acetate (Fluka) b.p. 97.8, n 1.3883. Purity (alkaline hydrolysis [9]) 99.8 ± 0.2 %

Analytical grade *toluene* (Baker) was used without purification.

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 1961 table of atomic weights.[10]

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* *Apparatus, Calibration, Calorimetric procedure* and *Correction to standard states*. See Ref.[8]

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

Donor	mmole	g $SbCl_5$	$10^4 \cdot \log R_i/R_f$	$-\Delta H$ kcal/mole
2-Butanone	1.495	1.51	66.34	17.83
$q = -0.03$ cal	1.505	1.26	67.00	17.87
	1.802	1.50	79.87	17.81
	2.886	1.58	127.32	17.74
	3.482	1.69	153.44	17.74
				17.80 ± 0.03
3-Methyl-2-butanone	1.059	1.23	45.99	17.42
$q = -0.02$ cal	1.455	1.21	62.95	17.37
	2.670	1.45	115.51	17.40
	2.882	1.46	125.18	17.47
	3.156	1.47	136.42	17.39
				17.41 ± 0.02
Pinacolin	0.553	1.34	23.76	17.25
$q = -0.01$ cal	1.178	1.38	50.25	17.15
	1.347	1.42	57.81	17.26
	1.787	1.36	76.22	17.16
	1.916	1.40	81.61	17.13
				17.19 ± 0.03
Ethyl propionate	1.093	0.89	46.54	17.08
$q = -0.01$ cal	1.630	1.49	69.13	17.05
	2.191	1.41	92.26	16.94
	2.775	1.58	117.28	17.02
	2.856	1.54	120.42	16.97
				17.01 ± 0.03
Ethyl isobutyrate	0.854	1.32	34.77	16.36
$q = 0.01$ cal	1.708	1.37	69.22	16.29
	1.825	1.26	74.20	16.35
	2.254	1.31	90.78	16.20
	2.299	1.30	93.25	16.32
				16.30 ± 0.03
Ethyl pivalate	1.154	1.24	36.72	12.78
$q = -0.01$ cal	1.212	1.44	38.46	12.75
	1.242	1.41	39.34	12.73
	3.350	1.69	105.67	12.72
				12.74 ± 0.02
t-Butyl acetate	1.173	1.22	105.23	36.05
	1.180	1.31	105.67	35.99
				36.0

RESULTS

The experimental results are summarized in Tables 1 and 2. The heat equivalent, ε°, of the system used was in all measurements 4012 ± 2 cal. per unit of log R_i/R_f. In the heat of reaction measurements (Table 1) the first column gives the name of the donor together with a sum correction, q, com-

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

Donor	mmole	$10^4 \cdot \log R_i/R_f$	$-\Delta H$ kcal/mole
2-Butanone	3.755	3.54	0.37
$q = -0.01$ cal	4.218	4.03	0.38
	4.280	4.00	0.37
			0.37 ± 0.00
3-Methyl-2-butanone	3.219	2.76	0.34
$q = 0.00$ cal	3.226	2.74	0.34
	3.318	2.79	0.34
			0.34 ± 0.00
Pinacolin	2.334	1.37	0.24
$q = 0.01$ cal	3.020	1.81	0.24
	3.258	1.92	0.24
			0.24 ± 0.00
Ethyl propionate	2.285	1.02	0.18
$q = 0.01$ cal	3.714	1.72	0.19
	3.810	1.80	0.19
			0.19 ± 0.00
Ethyl isobutyrate	2.024	0.16	0.03
$q = 0.00$ cal	2.751	0.20	0.03
			0.03 ± 0.00
Ethyl pivalate	2.451	−1.27	−0.20
$q = 0.01$ cal	3.610	−1.70	−0.19
	3.661	−1.69	−0.18
			−0.19 ± 0.01
t-Butyl acetate	2.669	0.79	0.12
	2.875	0.86	0.12
			0.12

pensating for a number of small heat effects.[8] Columns 2 and 3 give the amounts of donor and acceptor. The $SbCl_5$ was added in excess prior to the experiment to take care of traces of water inside the calorimeter and in the solvent. Column 4 gives the corrected temperature rise expressed in units of $10^4 \cdot \log R_i/R_f$, where R_i and R_f are the extrapolated initial and final thermistor resistances. The last column gives the molar enthalpy change.

In some cases it may seem that a slight trend exists in the data presented, *i.e.* somewhat higher results are obtained for smaller amounts of donor added. However, an analysis of the data in Ref.[8] and in this paper reveals that this trend is not statistically significant.

The heat of solution experiments (Table 2) were performed in pure ethylene chloride.

Table 3 gives the collected data from this paper and Ref.[8], *i.e.* the enthalpy changes calculated for the reaction occurring with both reactants and reaction products in ethylene chloride solution. For ethyl isobutyrate, the value given

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 ± 0.04
Me(Et)CO	17.80	0.37	17.43 ± 0.03
Me(*i*-Pr)CO	17.41	0.34	17.07 ± 0.03
Me(*t*-Bu)CO	17.19	0.24	16.95 ± 0.03
MeO(Me)CO *	16.60	0.22	16.38 ± 0.03
EtO(Me)CO *	17.32	0.24	17.08 ± 0.05
i-PrO(Me)CO *	17.69	0.16	17.53 ± 0.05
[*t*-BuO(Me)CO	36.0	0.12	35.9]
EtO(Et)CO	17.01	0.19	16.82 ± 0.03
EtO(Pr)CO *	16.85	0.09	16.76 ± 0.05
EtO(*i*-Pr)CO	16.30	0.03	16.44 ± 0.05
EtO(*t*-Bu)CO	12.74	−0.19	12.93 ± 0.03

* From Ref[8].

has been corrected for the presence of 1.0 ± 0.2 % toluene in the sample. The heat of solution of toluene in $SbCl_5$-ethylene chloride was determined experimentally. A slow exothermal reaction took place after the dissolution. A reaction period of four minutes was used, equal to the duration of the reaction period in the main experiments. The correction in $-\Delta H$ for 1 % toluene amounted to 0.14 kcal.mole^{-1}.

DISCUSSION OF RESULTS

Before a close examination of the data is attempted, it is necessary to stress the ambiguity of the results as far as the esters are concerned. Both the carbonyl oxygen and the ether oxygen could principally act as donors. As long as structure determinations (rigorously in the solution!) have not been carried out, the question of which oxygen atom acts as donor must in the individual case be regarded as unsettled. However, numerous infrared measurements give strong support to the idea that the carbonyl oxygen is in fact the donating atom. The formation of the adducts influences markedly the C=O stretching frequency, which decreases, whereas the carboxyl-carbon ether-oxygen frequency increases in agreement with the expectations. Were the ether oxygen the donating atom, the changes upon formation of adducts should be the opposite.[2]

The effect of a change in the alkoxy group when going from methoxy over ethoxy to isopropoxy is quite evident: the enthalpies of formation increase. This is in accordance with a multitude of experimental evidence (+ I effect [11]). Lindqvist *et al.* found this trend for the pair $(MeO)_3PO-(BuO)_3PO$,[2] and Osipov *et al.* have found from heat of mixing measurements an increase in enthalpy of formation of 0.8 kcal.mole^{-1} when going from isopentyl acetate to *sec.*-octyl acetate ($TiCl_4$ as acceptor).[3] On the other hand, these authors found a rather unexpected difference of 0.4 kcal.mole^{-1} between butyl- and isopentylformate. However, the limits of error in these measurements are not known.

When it comes to a discussion of the change in enthalpy of formation of the adducts accompanying a variation in the alkyl group directly attached to the carbonyl group, it will seem from a comparison between ethyl propionate and ethyl butyrate, that an increased chain length beyond two carbon atoms might be without any significant influence. On the other hand, an increased α-branching in the alkyl group changes the ΔH-values the effect being the opposite to that obtained for the alkoxy groups. The reason for this difference is obscure and will not be commented on, although an explanation is possible in terms of well-known effects like the inductive and the Baker-Nathan effect. One thing seems to be rather clear: it cannot be the result of steric repulsions between the alkyl group and the acceptor molecule. The steric requirement of a *t*-butyl group is much more pronounced than that of an ethyl group. Therefore, if steric effects were of primary importance, one should expect pinacolin to give a much lower heat of formation value for its adduct than methyl ethyl ketone.

As is seen from Table 3, the effect is small and of the same magnitude (although opposite in direction) as when the alkyl-group is attached one atom further away from the carbonyl group.

The difference in behaviour between pinacolin and ethyl pivalate is striking. The latter compound seems to exert a strong steric interaction; the decrease in $-\Delta H$ when going from ethyl isobutyrate to ethyl pivalate is 3.5 kcal. mole^{-1}. This effect could possibly be accounted for by considering the normal conformation of an ester. The $O-C_{alk}$ bond ordinarily is *cis* to the carbonyl bond and the temperature invariance of the dipole moment for an alkyl alkanoate indicates strong resistance towards rotation around the $C_{carboxyl}-O_{ether}$ bond (Ref. [12,p. 235]). However, model studies seem to reveal that the *cis*-conformation ought to give a steric repulsion between the alkoxy group and the octahedrically arranged chlorine atoms in the adduct. In adducts between *n*-alkanoates and $SbCl_5$, the alkoxy group may therefore be turned away from the *cis*-position. This is possible even in the ethyl isobutyrate adduct without creating interactions between the isopropyl and ethyl groups. In ethyl pivalate the tertiary butyl group of the acid prevents the O-alkyl group from attaining *trans* position. Only further systematic studies, however, can possibly elucidate the cause of the behaviour of ethyl pivalate versus pinacolin.

Acetone has a lower $-\Delta H$ value than methyl ethyl ketone. The reason for this is probably the same as that behind the results from ionization potential measurements on the two compounds. The electron donating ability of a molecular species ought to be parallelled by the ease with which it can split off an electron, quantitatively measured by its ionization potential. Electron impact experiments gave ionization potentials 9.89 and 9.74 eV for acetone and methyl ethyl ketone, respectively, and in photoionization the results 9.73 ± 0.01 and 9.69 ± 0.01 eV were obtained (Ref. [13,p. 14]). Unfortunately, ionization potential measurements are scarce and an interesting comparison with ΔH-values must await further experimental data.

Acknowledgement. A grant from the Faculty of Mathematics and Natural Sciences, University of Uppsala, is gratefully acknowledged.

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Received July 31, 1963.