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Heats of Formation of Adducts between Antimony Pentachloride and Substituted N,N-Dimethylamides

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Heats of formation of some 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 substituted N,N-dimethylamides were donors; the obtained heat of formation values in kcal.mole^{-1} are given within brackets: ethyldimethylcarbamate (22.37), N,N-dimethyltrifluoroacetamide (16.58), and dimethylcarbamylchloride (17.22).

This paper is the continuation of a systematic study of the effects upon the enthalpy of adduct formation of a variation in R in compounds of the general formula $R_1R_2C{=}O$. R_1 and R_2 are attached to the carbonyl group through either two of the elements carbon, nitrogen, oxygen, or chlorine. Refs. 1 and 2 cover cases in which carbon and oxygen are nearest neighbours and Ref. 4 gives further data on ketones to illustrate the effect of bulky substituents. This paper together with Ref. 3 give data on compounds where R_1 is a dimethylamino group and R_2 one of the following groups: methyl, trifluoromethyl, dimethylamino, ethoxy, or chlorine.

EXPERIMENTAL**

Materials

Ethylene chloride was treated as given in Ref. 1.

Analytical grade *antimony pentachloride* was distilled under reduced pressure in a carefully dried simple open column and collected in 20 ml break-off ampoules which were sealed off one by one and stored in the dark.

Ethyldimethylcarbamate was synthesized from ethylchloroformate and dimethylamine [5] and purified by distillation at reduced pressure. The purification was followed by analytical GLC using polyethyleneglycol on Chromosorb P as stationary phase. n_D^{25} 1.4137, d_4^{25} 0.9608.

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** *Apparatus, Calibration, Calorimetric Procedure* and *Correction to standard states,* see Ref. 1.

N,N-Dimethyltrifluoroacetamide was prepared from methyltrifluoroacetate and dimethylamine.[6] The amide was purified by distillation at reduced pressure and the purification was followed by GLC using polyethyleneglycol on Embacel as stationary phase. n_D^{25} 1.3610, d_4^{25} 1.2558. The water content of ethyldimethylcarbamate and dimethyltrifluoroacetamide was checked by a method using calcium hydride [7] and found to be less than 0.02 % (weight) in both cases.

Dimethylcarbamylchloride (Fluka) was dried with micro sieves and distilled at 3 mm Hg, b.p. 32°C. The purity was checked by titration after alkaline hydrolysis. The dimethylamine was boiled off, an excess of hydrochloric acid was added, CO_2 was boiled off, and the sample was then titrated. The purity was found to be 99.9 %, n_D^{25} 1.4510, d_4^{25} 1.1651.

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.[8]

RESULTS

The experimental results are summarized in Tables 1—3. Two different systems were used. System I with heat equivalent 3524 ± 2 cal per unit of log R_i/R_f and system II with heat equivalent 1115.0 ± 0.7 cal per unit of $2(R_i - R_f)/(R_i + R_f)$. Together with the change in the system a change has been made in the approximation of the function for the temperature dependence of the thermistor resistance.[9] The results of the heat of reaction measurements are shown in Table 1 where the first column gives the name of the donor together with a sum correction q, compensating for a number of small heat effects.[1] Columns 2 and 3 give the amounts of donor and acceptor. The $SbCl_5$ was added in excess prior to the experiment. Column 4 gives the corrected temperature rise expressed in units of 10^4 log R_i/R_f (I) or $10^2 \times 2(R_i - R_f)/(R_i + R_f)$ (II) where R_i and R_f are the extrapolated initial and final thermistor resistances, respectively. The last column gives the molar enthalpy change. The heat of solution experiments (Table 2) were performed in pure ethylene chloride. The data obtained are given in Table 3 together with the calculated values of the enthalpy change for the formation of the adducts in solution. Previously reported data for dimethylacetamide and tetramethylurea have been included in Table 3.

DISCUSSION OF RESULTS

As could be expected from the known inductive effects of the chlorine atom and the trifluoromethyl group the heats of adduct formation of dimethylcarbamylchloride and dimethyltrifluoroacetamide are of the same order of magnitude, 17.22 and 16.58 kcal.mole^{-1}, respectively. The inductive constants σ_I are + 0.47 for chlorine and + 0.41 for the trifluoromethyl group.[10] One could perhaps expect the reverse order for the heat of formation values. It is possible that the slightly greater steric requirements of the trifluoromethyl group compared to chlorine is the reason for the lower value of the amide. Previous work [4] suggests that the heats of formation of the adducts are sensitive to changes in the size of the groups attached to the carbonyl group. A steric effect could be of two types: either it could give a direct interaction with the

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

Donor	mmole	g $SbCl_5$	$10^4 \times \log R_i/R_f$ (I) $10^2 \times 2 \times (R_i - R_f)/(R_i + R_f)$ (II)	$-\Delta H$ kcal/mole
Ethyldimethylcarbamate (I)	0.686	1.22	44.45	22.87
	0.757	1.19	49.12	22.89
$q = 0.00$	1.391	1.41	89.42	22.71
	1.469	1.48	94.57	22.75
	1.575	1.48	101.30	22.73
				22.79 ± 0.03
Dimethyltrifluoroacetamide (I)	0.708	1.49	32.68	16.30
	1.293	1.40	59.84	16.36
$q = 0.00$	1.318	1.32	60.71	16.27
	1.662	1.42	76.52	16.27
	1.678	1.59	77.44	16.33
				16.31 ± 0.02
Dimethylcarbamylchloride (II)	1.006	2.00	1.571	17.53
	1.309	1.46	2.048	17.53
$q = 0.03$	1.472	1.46	2.301	17.52
	2.172	1.66	3.396	17.54
				17.53 ± 0.01

chlorine atoms in the antimony pentachloride, or it could hinder the planarity of the amide molecule and thus reduce the π-bonding in the C—N bond which would give a lower electron density at the oxygen atom. Differences in solute-solvent interactions could also have an effect on heat of formation values.

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

Donor	mmole	$10^4 \times \log R_i/R_f$ (I) $10^2 \times 2 \times (R_i - R_f)/(R_i + R_f)$ (II)	$-\Delta H$ kcal/mole
Ethyldimethylcarbamate (I)	1.444	1.62	0.41
$q = 0.02$	2.067	2.42	0.42
	2.166	2.53	0.42
			0.42 ± 0.00
Dimethyltrifluoroacetamide (I)	2.563	−2.08	−0.29
$q = 0.02$	2.799	−2.18	−0.27
	3.847	−2.98	−0.27
			−0.27 ± 0.01
Dimethylcarbamylchloride (II)	1.418	0.037	0.31
$q = 0.03$	2.305	0.062	0.31
	3.138	0.085	0.31
			0.31 ± 0.00

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

Donor	$-\Delta H_1$ kcal.mole^{-1}	$-\Delta H_2$ kcal.mole^{-1}	$-\Delta H$ kcal.mole^{-1}
$Me_2N(Me)CO$*	28.71	0.91	27.80 ± 0.08
$(Me_2N)_2CO$*	30.69	1.05	29.64 ± 0.03
$Me_2N(C_2H_5O)CO$	22.79	0.42	22.37 ± 0.03
$Me_2N(CF_3)CO$	16.31	−0.27	16.58 ± 0.02
$Me_2N(Cl)CO$	17.53	0.31	17.22 ± 0.01

* From Ref. 3.

As seen from the results the —I effect of the chlorine atom and the trifluoromethyl group balances the positive π-bonding effect of the dimethylamino group, the $-\Delta H$ values being approximately the same for dimethylcarbamylchloride and dimethyltrifluoroacetamide as for an ordinary ketone,[1] (*e.g.* acetone 17.07 kcal.mole^{-1}). A closer comparison cannot be made due to the complexity of the initial and final states of the adduct formation reaction. Middaugh *et al.*[11] obtained the same $-\Delta H$ values, 3.0 kcal.mole,$^{-1}$ for the much weaker complexes of dimethyltrifluoroacetamide and acetone with phenol as acid.

The replacement of the C-methyl group in N,N-dimethylacetamide by an ethoxy group to give ethyldimethylcarbamate leads to a decrease in the $-\Delta H$ value from 27.80 to 22.37 kcal.mole^{-1}. This change fits approximately a linear relationship between $-\Delta H$ and σ_I values according to Fig. 1.* The σ_I value for a methoxy group is + 0.25 and the value for an ethoxy group is assumed to be the same.

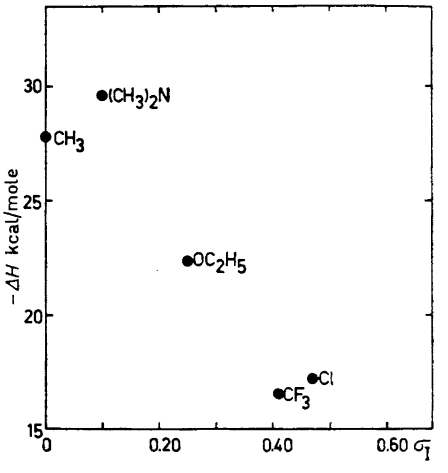

Fig. 1. Plot of heat of formation of $(CH_3)_2$ NCOR adducts against σ_I of R.

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* The effect of introducing an alkoxy group into an ester will be commented on in a later paper.

The lowering of the $-\Delta H$ values for substituted N,N-dimethylamides when going from methyl to ethoxy is 5.4 kcal. and from methyl to chlorine 10.6 kcal. Thus the ethoxy group with its possibility of conjugation with the carbonyl group seems not to give any appreciable contribution to the electron density at the oxygen atom in ethyldimethylcarbamate.

Tetramethylurea has a $-\Delta H$ value of 29.64 kcal.mole^{-1} which is 1.8 kcal higher than that of dimethylacetamide although the σ_I value for the dimethylamino group is $+ 0.10$. If it is assumed that a $-$I effect can be treated separately from a π-bonding effect then the replacement of the C-methyl group with a second dimethylamino group in dimethylacetamide would lead to a decrease of about 2 kcal as judged from Fig. 1. That means that an effect of π-bond interaction on the $-\Delta H$ value of about 4 kcal can be ascribed to the second dimethylamino group in tetramethylurea. On the other hand the difference in heat of adduct formation values between an ordinary ketone and dimethylacetamide is about 11 kcal.mole^{-1}. Assuming that the $-$I effect can still be taken as about 2 kcal, then the introduction of the first dimethylamino group gives a π-bond interaction effect of about 13 kcal. mole^{-1}. The difference in π-bond interaction between the first and the second dimethylamino group is probably caused by two effects. In the first place, the π-bond interaction of the second dimethylamino group is hampered by the already existent delocalization in the first amino group.[12] Secondly, as Middaugh *et al.* have pointed out, the tetramethylurea cannot be planar due to steric interactions between the methyl groups.*

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* In a recent paper[13] the rather doubtful result was reported that the skeleton in tetramethylurea is very nearly coplanar at a N—C—N angle of 120°.