reflect differences in the entropies of activation. It is not uncommon to find systems for which "corrections" to rate constants, due to steric or statistical effects, must be made. It is often unclear how to best make these corrections. Furthermore, in order to compute k_{1p} from the measured rate constant, one must estimate K_{os}', which may be subject to substantial errors for the interaction of highly charged partners. The temperature dependence of K_{os}', on the other hand, is usually quite small. As a consequence, the numerical value of $\Delta H_{1p}^{\ddagger}$ may be a more reliable criterion of the type of substitution mechanism.

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A Comparison between Enthalpies of Formation of Antimony Pentachloride Adducts in Carbon Tetrachloride and in 1,2-Dichloroethane Solution[1]

Gerd Olofsson* and Inger Olofsson

Contribution from the Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden. Received April 6, 1973

Abstract: Enthalpies of formation in carbon tetrachloride solution of molecular adducts between antimony pentachloride and eight oxygen compounds of varying donor strengths have been determined calorimetrically. They are compared with earlier reported enthalpies of adduct formation in 1,2-dichloroethane. A satisfactory linear relation was observed between the two sets of values, and none of the systems studied indicated any irregular solvation interaction in 1,2-dichloroethane.

In thermodynamic studies of donor–acceptor interactions experimental conditions are sought that will allow found values to be interpreted in terms of changes in intramolecular energies of reactant and product molecules. As gas phase reactions can be realized only in a very few cases, donor–acceptor interactions must generally be studied in solutions. It becomes a prerequisite to minimize disturbing influences of intermolecular interaction. The requirements that the solvent must keep reactants and products in solution and at the same time give negligible solute–solvent interaction contributions are conflicting, and solvents like *n*-heptane and cyclohexane, which are considered to give small solvation contributions, find a limited use in studies of systems giving polar adducts.

The good solvating properties of 1,2-dichloroethane and its chemical inertness and moderately low vapor pressure at room temperature make it a useful solvent for studies of strong donor–acceptor interactions in solution.[2–4] The usability of this solvent has, however, been questioned by Drago and coworkers[5,6] who hold the opinion that "1,2-dichloroethane should be avoided as a solvent for studies of acid–base interaction because of extensive and unpredictable contributions to the enthalpies of adduct formation from solvation." Their statement is based on discussions of formation enthalpies of donor–acceptor adducts of $SbCl_5$[5] and of hydrogen-bonded complexes of *m*-fluorophenol.[6] The discussion of solvent effects in the formation of $SbCl_5$ adducts was based on results of measurements on two systems in both CCl_4 and $1,2\text{-}C_2H_4Cl_2$ and the remaining part on merely estimated values. Neither do the results of the study of five hydrogen-bonded systems in various solvents give evidence of "unpredictable" solvation contributions in $1,2\text{-}C_2H_4Cl_2$. It can be seen from plots that the assumption of a linear relation between enthalpy changes measured in $1,2\text{-}C_2H_4Cl_2$ and in CCl_4 or $o\text{-}C_6H_4Cl_2$ gives a satisfactory description of the reported results, the maximum deviation being about 1.5 kJ mol^{-1} (0.4 kcal mol^{-1}). The observed effect is in our opinion not large enough to discourage the use of $1,2\text{-}C_2H_4Cl_2$. We found it to be of interest to compare enthalpy changes in $1,2\text{-}C_2H_4Cl_2$ with values observed in CCl_4 for a number of adducts with as widely varying donor strength as possible to gain further information about solute–solvent interactions in $1,2\text{-}C_2H_4Cl_2$. The use of the strong Lewis acid $SbCl_5$ as the reference acid gives complete conversion to adduct in the calorimetric experiment for a large range of strengths of interaction which reduces the experimental errors in the measured enthalpy changes.

Experimental Section

Materials. Antimony pentachloride was treated as reported.[7] It was transferred from the storage ampoules by suction in an atmosphere of dry nitrogen to 1-ml glass pipettes which were sealed. 1,2-Dichloroethane (Fisher Certified ACS grade) was fractionally distilled before use. Carbon tetrachloride (BDH, ANALAR quality) was used eithout further purification. The solvents were stored over molecular sieves 4A and the water content of the calori-

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[1] This work was supported by a grant from the Swedish Natural Science Research Council.

[2] I. Lindqvist and M. Zackrisson, *Acta Chem. Scand.*, **14**, 453 (1960).

[3] G. Olofsson, *ibid.*, 22, 377 (1968), and references therein.

[4] V. Gutmann and H. Czuba, *Monatsh. Chem.*, **100**, 708 (1969), and references therein.

[5] Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 202 (1972).

[6] M. S. Mozari and R. S. Drago, *J. Amer. Chem. Soc.*, **94**, 6877 (1972).

[7] G. Olofsson, *Acta Chem. Scand.*, **21**, 93 (1967).

Table I. Enthalpies of Solution of Donor Compounds and Enthalpies of Formation of $SbCl_5$ Adducts Measured in CCl_4 and $1,2\text{-}C_2H_4Cl_2$

Donor compd	CCl_4		$1,2\text{-}C_2H_4Cl_2$	
	$-\Delta H$(soln), kJ mol^{-1}	$-\Delta H$, kJ mol^{-1}	$-\Delta H$(soln), kJ mol^{-1}	$-\Delta H$, kJ mol^{-1}
Ethyl dimethylcarbamate[a]	1.06 ± 0.02	83.8 ± 0.2	1.74 ± 0.02[b]	95.4 ± 0.2[b]
Tetrahydrofuran	2.51 ± 0.02	80.8 ± 0.5	1.71 ± 0.00[c]	88.0 ± 0.2[c]
Dipropyl ether	1.00 ± 0.08	68.8 ± 0.1	-2.56 ± 0.01[d]	74.6 ± 0.2[d]
Methyl propyl ketone	-1.34 ± 0.02	67.4 ± 0.1	1.17 ± 0.01[e]	73.2 ± 0.2[e]
Ethyl acetate	-0.21 ± 0.00	66.5 ± 0.1	1.00 ± 0.00[f]	71.5 ± 0.2[f]
1,2-Propanediol carbonate	-13.75 ± 0.05[g]	58 ± 1[g]	0.33 ± 0.01[h]	62.4 ± 0.3[h]
Ethyl monochloroacetate	-5.02 ± 0.00	53.6 ± 0.3	0.26 ± 0.01[i]	53.6 ± 0.1[i]
Nitrobenzene	-4.83 ± 0.02	36 ± 2[j]	-0.43 ± 0.02	34 ± 3[j]

[a] Strongest donor studied. The adducts of the following donors were not soluble enough in CCl_4: dimethyl sulfoxide, dimethylacetamide, tetramethylurea, trihexylamine, and octylamine. [b] From ref 7. ΔH checked with present sample. [c] V. Gutmann and A. Scherhaufer, *Monatsh. Chem.*, **99**, 335 (1968), give 1.3 and 83.7 kJ mol^{-1}, respectively, without stating the uncertainty of the measurements. [d] G. Olofsson, *Acta Chem. Scand.*, **22**, 1352 (1968). [e] G. Olofsson, *ibid.*, **21**, 2415 (1967). [f] From ref 9. ΔH checked with present sample. [g] At 40°. See text. [h] V. Gutmann, F. Mairinger, and H. Winkler, *Monatsh. Chem.*, **96**, 574 (1965), give 0.4 and 63.2 kJ mol^{-1}, respectively, without stating the uncertainty of the measurements. [i] G. Olofsson, *Acta Chem. Scand.*, **21**, 1892 (1967). [j] See text.

metric liquid could in this way be kept below 10 ppm as judged from gsc.[8] The sample of ethyl *N,N*-dimethylcarbamate has been described previously.[7] The commercially available donor compounds, usually of analytical grade, were further purified by fractional distillation. The purity of the samples was checked by analytical glc and found to be better than 99.5% for ethyl dimethylcarbamate and dipropyl ether and better than 99.8% for the other compounds. The samples were dried with molecular sieves 4A. The water content was checked separately by gsc[8] and found to be less than 0.01% in the samples used.

Apparatus. The calorimetric measurements were made with an LKB 8721 reaction solution calorimeter using glass reaction vessels of 25- and 100-ml volume. Calorimetric procedure and corrections to standard states are described in ref 9.

The results of the calorimetric measurements are expressed in terms of absolute joules and refer to the isothermal process at 25° and to the true mass.

Results

The results of the calorimetric measurements are summarized in Table I. ΔH(soln) denotes the enthalpy change for the dissolution of the liquid donor in the solvent to give a 0.01 to 0.04 mol l.$^{-1}$ solution. The observed values for 1,2-propanediol carbonate in CCl_4 were, however, concentration dependent, and the given value was therefore derived by linear extrapolation to zero concentration.

ΔH denotes the enthalpy change for the following reaction.

$$\mathrm{D(soln)} + \mathrm{SbCl_5(soln)} \longrightarrow \mathrm{D\cdot SbCl_5(soln)} \qquad (1)$$

Previously reported results from measurements with $1,2\text{-}C_2H_4Cl_2$ as the solvent are included in the table.

The experiments with 1,2-propanediol carbonate in CCl_4 were carried out at 40° as the adduct was somewhat more soluble at this temperature. The larger error limit assigned for this system stems from difficulties in varying the concentration of the reactants enough to ensure that there was complete conversion to adduct in the experiments.

The enthalpy changes for the formation of the ethyl dimethylcarbamate and ethyl acetate adducts in both CCl_4 and $1,2\text{-}C_2H_4Cl_2$ at 40° were within experimental error the same as those observed at 25°. It can be concluded that ΔC_p for the adduct formation reaction 1 is very small.

The association constant and enthalpy change for the formation of the $C_6H_5NO_2\cdot SbCl_5$ adduct were derived simultaneously from results of measurements with varying concentrations of the reactants; $c(C_6H_5NO_2)$ from 0.01 to 0.07 mol l.$^{-1}$ and $c(SbCl_5)$ from 0.03 to 0.2 mol/l.$^{-1}$. One series of eight experiments was made in $1,2\text{-}C_2H_4Cl_2$ and two series in CCl_4. A K value of 20 ± 3 l. mol^{-1} was found in the former solvent and a value of 10 ± 1 l. mol^{-1} in CCl_4. The corresponding ΔH values are shown in Table I. For the evaluation of the values of the parameters the sum of the square of the differences between observed and calculated enthalpy changes was calculated for an array of K and ΔH values using a Univac 1108 computer.

The given error limits indicate random errors expressed as twice the standard deviation of the mean. The uncertainty in the K and ΔH values of $C_6H_5NO_2\cdot SbCl_5$ were estimated from the variation of the square error sum with the parameter values.

In Figure 1 the enthalpies of adduct formation in $1,2\text{-}C_2H_4Cl_2$ are plotted against the values obtained in CCl_4. Least-squares fitting of the points to a straight line gives the line indicated in Figure 1.

Discussion

Calorimetrically determined enthalpy changes for adduct formation reactions in solution, *cf.* reaction 1, can be regarded as the sum of two terms

$$\Delta H = \Delta H(\mathrm{g}) + \Delta H(\mathrm{ext}) \qquad (2)$$

where ΔH(g) represents the gas phase enthalpy of adduct formation and ΔH(ext) represents the enthalpy contribution from solute–solvent interactions essentially electrostatic in origin in the systems under consideration. ΔH(ext) will be zero only in those cases where the sum of the solvation enthalpies of the reactants equals the solvation enthalpy of the product.[10] Molecular properties of the solvent molecules such as dipole moment, polarizability, and geometry will determine the solute–solvent interaction energies. In the reaction between a strong nonpolar Lewis acid and a polar organic donor the dipole moment of the adduct formed is usually larger than that of the unbound donor.[11,12] The adduct can be expected to interact more strongly with the solvent than the donor and ΔH values measured in polar solvents can therefore include exothermal contributions from solute–solvent inter-

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(8) P. Sellers, *Acta Chem. Scand.*, **25**, 2295 (1971).

(9) G. Olofsson, I. Lindqvist, and S. Sunner, *ibid.*, **17**, 259 (1963).

(10) The solvation enthalpy of species A is defined as the enthalpy change for the process A(g) → A(soln).

(11) I. Lindqvist, "Inorganic Adduct Molecules of Oxo-compounds," Springer-Verlag, Berlin, 1963, p 78.

(12) E. N. Gur'yanova, *Russ. Chem. Rev.*, **37**, 863 (1968).

actions. It is also possible that in not too strongly bound adducts a decrease in solvation energy due to reduced accessibility of the polar group in the donor will not be compensated for by the increase in solvation arising from the formation of the polar donor–acceptor bond. In such cases the unbound donor can be more effectively solvated than the adduct and an endothermal solvation contribution will be found. Measured ΔH values can be assumed to reflect intrinsic properties of reactant and product molecules provided that ΔH(ext) varies monotonically with ΔH(g).

The dielectric constant of $1,2\text{-}C_2H_4Cl_2$ is 10.36 while that of CCl_4 is 2.23 at 25°,[13] and many donor–acceptor systems which are not accessible for measurements in CCl_4 solution are soluble enough to be studied in $1,2\text{-}C_2H_4Cl_2$ solution. Neither solvent shows any noticeable tendency to act as Brønsted or Lewis acid or base. Solvation contributions to enthalpy changes measured in CCl_4 are generally considered to be small. The rather large endothermal enthalpy change for the dissolution of 1,2-propanediol carbonate in CCl_4, 13.75 kJ mol^{-1}, shows that solute-solvent interactions in this case do not compensate for the loss in solute–solute interactions present in the liquid donor. The strong dipole–dipole interaction in liquid 1,2-propanediol carbonate (molecular weight 102.1) is reflected in its large enthalpy of vaporization, 59.6 ± 0.5 kJ mol^{-1},[14] and high boiling point, 240°. The corresponding values for, *e.g.*, ethyl acetate (molecular weight 88.1), are 35.2 ± 0.2 kJ mol^{-1} [15] and 77°, respectively. For the latter donor the loss in intermolecular interaction in the liquid is compensated for by solute–solvent interactions in CCl_4 solution.

The results of the measurements of enthalpies of formation of $SbCl_5$–oxygen donor adducts in the two solvents, Table I, show that there are substantial exothermal contributions in $1,2\text{-}C_2H_4Cl_2$ relative to CCl_4 to the ΔH values of the strong adducts of ethyl dimethylcarbamate and tetrahydrofuran. The influence of $1,2\text{-}C_2H_4Cl_2$ becomes smaller for the less strongly bound adducts and equal ΔH values are observed for ethyl monochloroacetate. However, as can be seen from Figure 1, there is a satisfactory linear relation between ΔH values measured in the two solvents. It is for instance noticeable how well the small differences between the adduct formation enthalpies in CCl_4 of methyl propyl ketone, ethyl acetate, and dipropyl ether are reproduced in $1,2\text{-}C_2H_4Cl_2$. Thus, for the systems studied the assumption that $\Delta H(1,2\text{-}C_2H_4Cl_2)$ will vary linearly with $\Delta H(CCl_4)$ is sufficient to rationalize solute–solvent interactions in $1,2\text{-}C_2H_4Cl_2$.

It has been suggested that the existence of two rotational isomers of $1,2\text{-}C_2H_4Cl_2$, the polar gauche and the nonpolar trans isomers, might complicate solute–solvent interactions in this solvent.[6,16] The two isomers have the same energy in the pure liquid and the gauche–trans ratio (N_g/N_t) has been estimated to be 1.3/1.[17] It is possible that polar solutes can induce an increase in the N_g/N_t ratio in the near vicinity of the solute molecules and thus make the effective dielectric constant greater than the macroscopic dielectric constant of the solvent.[18] However, this would give an additional solvation contribution that would be proportional to the main part of the solute–solvent interaction energy. It can be concluded that for the systems in the present study discussions of variations in relative strengths of interaction based on results of measurements in $1,2\text{-}C_2H_4Cl_2$ are equally as valid as those on results from CCl_4 solutions. The nonnegligible solvation contributions in $1,2\text{-}C_2H_4Cl_2$ ought not to be regarded as a peculiar property of $1,2\text{-}C_2H_4Cl_2$ but a consequence of its capability to act as the solvent for polar solutes. The risk for irregular solvation effects seems to have been overrated and the disadvantages of using $1,2\text{-}C_2H_4Cl_2$ as solvent have been exaggerated.

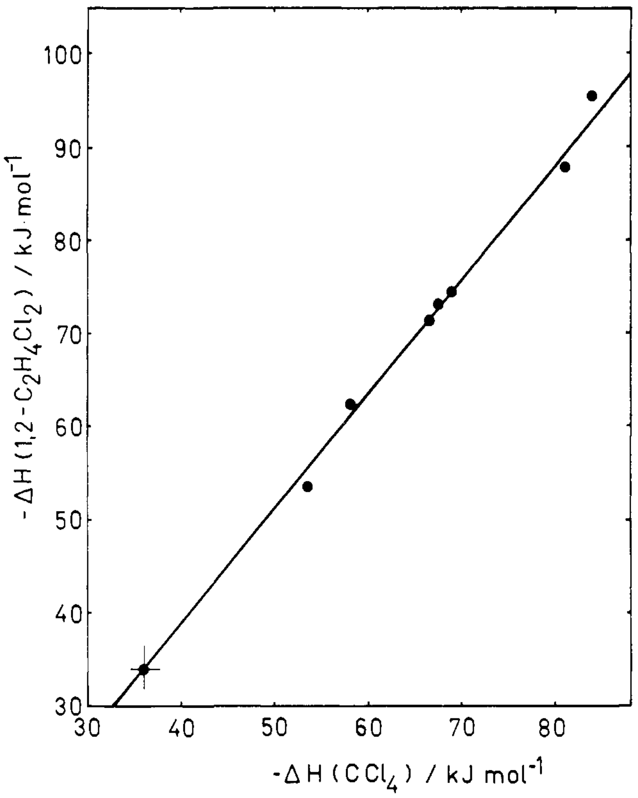

Figure 1. Enthalpies of formation of $SbCl_5$ adducts in $1,2\text{-}C_2H_4Cl_2$ against enthalpy changes measured in CCl_4.

In a recent paper[19] "an elimination of solvent procedure (ESP)" is described which according to the authors "enables one to study donor–acceptor reactions in polar solvents and predict, from these data, an enthalpy of the adduct formation in the gas phase." This procedure consists, however, merely of the assumption that for a series of adducts of a reference acid in a given solvent the difference between the solvation energy of the adduct and that of the unbound donor is constant. From the above comparison of ΔH values measured in $1,2\text{-}C_2H_4Cl_2$ with values observed in CCl_4, it is clear that this assumption will be of limited applicability and that this approach to treat solute–solvent interactions in polar solvents is unduly narrow.

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(13) A. A. Maryott and E. A. Smith, *Nat. Bur. Stand.* (*U.S.*), *Circ.*, No. 514 (1951).

(14) Unpublished result.

(15) I. Wadsö, *Acta Chem. Scand.*, **20**, 544 (1966).

(16) B. Nelander, *ibid.*, 20, 2289 (1966); B. Nelander, *ibid.*, 26, 809 (1972).

(17) S.-I. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954, Chapter II.

(18) An analogous phenomenon has been observed in studies of electrolyte solutions which show that the N_g/N_t ratio in $1,2\text{-}C_2H_4Cl_2$ in the near vicinity of ions is greater than it is in the pure solvent. Y. H. Inami and J. B. Ramsey, *J. Chem. Phys.*, 31, 1297 (1959).

(19) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, **64**, 90 (1972); *cf.* ref 6.