A Calorimetric Study of the Donor Properties of

N,N'-Methylureas

GERD OLOFSSON

Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

Enthalpies of formation of donor-acceptor adducts between antimony pentachloride and *sym*-dimethylurea (-124.1), trimethylurea (-122.6), and dimethylethyleneurea (-115.8) have been determined with both reactants and reaction product in ethylene chloride solution. The found enthalpy values in kJ mol^{-1} are given within brackets. Together with the previously determined value for tetramethylurea (-124.0) they show that steric repulsion between the methyl groups within the tetramethylurea molecule does not lower its donor ability.

Non-bonded interactions between donor and acceptor molecules are not significant in the adduct formation between methylsubstituted ureas and antimony pentachloride.

U rea has been shown to have a completely planar structure in the solid state.[1] In the mono-, di-, and tri-methylsubstituted ureas a planar configuration is still possible, but in tetramethylurea the steric requirements of the methyl groups prevent the molecule from having a planar $C_2NC(O)NC_2$ skeleton with an $N-C-N$ bond angle of $120°$. An attempt to estimate the influence of a nonplanar configuration on the π-bond interaction in tetramethylurea has been made by Middaugh *et al.*[2] If there exists a pronounced difference in π-bond interaction between alkylureas that can have a planar configuration and those who are nonplanar, this would give differences in the electron densities at the carbonyl oxygen atom and thus influence the electron pair donor ability of the molecules. Values of the enthalpy changes for the formation of adducts between antimony pentachloride and *sym*-di-, tri-, and tetramethylurea would reveal variation of that kind in the donor strength.

EXPERIMENTAL

Materials

sym-Dimethylurea (Fluka AG) was dried over P_2O_5 and sublimed under vacuum. *1,1,3-Trimethylurea* was synthesized from methylisocyanate and dimethylamine, fractionally distilled at reduced pressure, dried over P_2O_5 and sublimed under vacuum.

A melting point of 73.8°C was derived from the DSC melting curve. The purity of the solid samples was determined by analysis of the shape of melting peaks obtained by differential scanning calorimetry. Both samples were found to have purities of 99.8 ± 0.1 mol %.[3]

The purity of N,N'-*dimethyl-2-imidazolidone* (dimethylethyleneurea)* was checked by analytical GLC using Carbowax and dioctylphthalate as stationary phases and by PMR analysis. The impurities, excluding water, were judged to amount to less than 0.5 mole %. The water content of the sample was checked separately by a gas chromatographic method [4] and found to be 0.09 ± 0.01 %.

The substances, which are fairly hygroscopic, were handled in an atmosphere of dry nitrogen.

Ethylene chloride was treated as given in Ref. 5, and *antimony pentachloride* as given in Ref. 6.

A p p a r a t u s

The calorimetric experiments were carried out in an LKB 8721 Reaction Solution Calorimeter. The calorimeter is of the constant-temperature-environment type, and a thermistor is used as temperature senso.·. Glass reaction vessels of 100 and 25 ml volume were used.

Melting curves were obtained by a Perkin-Elmer Differential Scanning Calorimeter model DSC-1B. The PMR spectra were recorded on a Varian A60 spectrometer.

C a l o r i m e t r i c   p r o c e d u r e

The calorimeter was charged with 100.7 ml of ethylene chloride and 3×10^{-3} mol of $SbCl_5$ for the reaction experiments. The smaller vessel charged with 26.0 ml ethylene chloride was used in addition for the solution experiments. After equilibration the reaction was started by breaking the sealed glass ampoule containing about 5×10^{-4} mol of the donor compound. The reaction period was less than 3 min for trimethylurea and dimethylethyleneurea, but about 8 min for the less soluble dimethylurea. Corrected resistance values (R_i and R_f) were computed by extrapolating the fore and after periods to the time corresponding to 63 % of the resistance change (Dickinson's extrapolation method). The Regnault-Pfaundler method was used in addition for dimethylurea, but gave the same result as the extrapolation method. For the electrical calibrations, extrapolations were taken to the time corresponding to 50 % of the resistance change. The expression $(R_i - R_f)/(R_i + R_f)$ was used as being proportional to the temperature change.

Corrections to standard states. (See Ref. 7.) The results of the calorimetric experiments refer to the isothermal process at 25°C and to the true mass.

RESULTS

The results of the calorimetric experiments, three in each series, are given in Table 1 together with results of the adduct formation of tetramethylurea reported in Ref. 8. The first column gives the formula of the donor, and the second the enthalpy of reaction between liquid or solid donor and $SbCl_5$ in ethylene chloride solution. The enthalpy of solution of donor is given in the third column, and the fourth column states the calculated value of the enthalpy change for the reaction with both reactants and reaction product in ethylene chloride solution.

The enthalpies of solution of the solid alkylureas were measured in the con-

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* A sample of dimethylethyleneurea was kindly provided by Professor S. Forsén, Division of Physical Chemistry, Lund Institute of Technology, Chemical Center, Lund.

Table 1. Enthalpy changes accompanying the formation of adducts between SbCl$_5$ and various ureas in ethylene chloride solution.

	$-\Delta H_1/\text{kJ mol}^{-1}$	$-\Delta H_2/\text{kJ mol}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$
(MeNH)$_2$CO	100.03 ± 0.17	-24.10 ± 0.16	124.1 ± 0.2
MeNC(O)NMe	120.39 ± 0.05	4.15 ± 0.02	115.8 ± 0.3
| | CH$_2$ – CH$_2$			
Me$_2$N(MeNH)CO	100.20 ± 0.05	-22.39 ± 0.03	122.6 ± 0.1
(Me$_2$N)$_2$CO^a	128.41 ± 0.13	4.39 ± 0.04	124.0 ± 0.2

^{a} From Ref. 8.

centration range $0.004 - 0.015$ mol l^{-1} and found to be constant. The value in the last column for dimethylethyleneurea has been corrected for the presence of 0.09 % of water, assuming the density of the donor to be 1.0 g ml^{-1} and all water to react with SbCl$_5$ to give an enthalpy change of -78 kJ/mol.* The error limits are expressed as the single standard deviation of the mean.

DISCUSSION

It seems reasonable to assume that at least in adducts, the configuration of tetramethylurea resembles that of tetramethylthiourea, as it has been found in a recent determination of the structure of solid molecular adducts (C$_5$H$_{12}$N$_2$S)$_2$ TeX$_4$, (X=Br, Cl).[9],[10] The N – C – N bond angle is within limits of experimental errors 120°, and the steric repulsion between the methyl groups is overcome by twisting the dimethylamino groups about $20 - 30°$ out of the N – C(S) – N plane. The nitrogen atoms lie very nearly in the plane of the three carbon atoms bounded to them. The configuration of the nitrogen atoms is most probably planar also in solid tetramethylthiourea, contrary to what is reported by Žvonkova *et al.*[11] Vilkov *et al.*[12] repeated the calculations of the tetramethylthiourea molecule parameters on the basis of atomic coordinates given in Ref. 11, and they found almost coplanar nitrogen atoms. It will seem that the main difference between free and complexed tetramethylthiourea consists in changes of bond lengths in the vicinity of the thiocarbonyl group, but that other structural parameters are fairly unaltered by adduct formation. The same may also be true for tetramethylurea.**

In *sym*-dimethyl- and trimethylurea a planar C$_{1(2)}$NC(O)NC skeleton can be attained by placing the methyl substituent in one methylamino group *cis* to the carbonyl oxygen atom. π-Bond interaction between the nitrogen atoms and the carbonyl group will be at maximum for a planar skeleton and would diminish with increasing deviation from a planar structure. The calorimetric experiments do not reveal any difference in donor ability between

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* Unpublished result. The $-\Delta H$ value given in Ref. 5 is 24 kJ mol^{-1} too high.
** The statement in Ref. 12, that the tetramethylurea skeleton is very nearly coplanar at an N – C – N angle of 120° seems questionable.

sym-dimethyl-, trimethyl-, and tetramethylurea. On the contrary, they show the same donor strength towards antimony pentachloride as it is expressed in enthalpies of adduct formation (Table 1). The inductive effect of the methyl group can be assumed to be small (cf. Ref. 13), in any case it cannot cause great changes in the electron density at the oxygen atom. It can be concluded that there is no pronounced loss of π-bond interaction in tetramethylurea due to steric repulsion between methyl groups within the molecule.

The adduct formation between antimony pentachloride and dimethyl-ethyleneurea is $6-8$ kJ mol^{-1} less exothermic than adduct formation of the methyl substituted ureas which may reflect a difference in strength of donor-acceptor interaction. The effect on the donor ability of dimethylethyleneurea of changes in bond angles at the carbonyl carbon atom in the 5-membered ring can be expected to be small as γ-butyrolactone [13] and propandiol-1,2-carbonate [14] give the same enthalpy changes upon adduct formation as the corresponding open chain compounds.[7] In the sym-dimethylurea adduct one hydrogen atom may occupy a position cis to the carbonyl bond, and an adduct could form which is free from direct steric interactions, while steric repulsion between a methyl group in the donor and chlorine atoms in the acceptor could be expected to be accentuated in the dimethylethyleneurea adduct, since the two methyl groups must be cis to the oxygen atom and lie in the plane of the molecule. The series of enthalpy values given in Table 1 indicate that non-bonded interactions between donor and acceptor molecules are not significant in the adduct formation between methylsubstituted ureas and antimony pentachloride. Only in the dimethylethyleneurea adduct the steric effect may be, to a small extent, in operation.

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