A Calorimetric Study of the Donor Properties of $N,N'$-Methylureas

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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.

Urea 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 $C_3$NC(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 $\pi$-bond interaction in tetramethylurea has been made by Middaugh et al.$^2$ If there exists a pronounced difference in $\pi$-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.

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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 %. The purity of N,N'-dimethyl-2-imidazolidone (dimethylethylenurea) 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 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.

Apparatus

The calorimetric experiments were carried out in an LKB 8721 Reaction Solution Calorimeter. The calorimeter is of the constant-temperature-environment type, and a thermometer is used as temperature sensor. 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.

Calorimetric procedure

The calorimeter was charged with 100.7 ml of ethylene chloride and 3 x 10⁻² mol of SbCl₅ 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 x 10⁻⁴ mol of the donor compound. The reaction period was less than 3 min for trimethyleneurea and dimethylethylenurea, but about 8 min for the less soluble dimethyleurea. Corrected resistance values (R₁ and R₂) 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-Pfandler method was used in addition for dimethyleurea, 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 (R₁ - R₂)/(R₁ + R₂) 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 tetramethyleneurea 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 SbCl₅ 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 alkyleneureas were measured in the con-

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

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Table 1. Enthalpy changes accompanying the formation of adducts between SbCl₃ and various ureas in ethylene chloride solution.

<table>
<thead>
<tr>
<th>Adduct</th>
<th>$-\Delta H_1$/kJ mol⁻¹</th>
<th>$-\Delta H_2$/kJ mol⁻¹</th>
<th>$-\Delta H$/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MeNH)₂CO</td>
<td>100.03 ± 0.17</td>
<td>-24.10 ± 0.16</td>
<td>124.1 ± 0.2</td>
</tr>
<tr>
<td>MeNC(O)NMe</td>
<td>120.39 ± 0.05</td>
<td>4.15 ± 0.02</td>
<td>115.8 ± 0.3</td>
</tr>
<tr>
<td>CH₄−CH₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me₂N(MeNH)₂CO</td>
<td>100.20 ± 0.05</td>
<td>-22.39 ± 0.03</td>
<td>122.6 ± 0.1</td>
</tr>
<tr>
<td>(Me₂N)₂CO</td>
<td>128.41 ± 0.13</td>
<td>4.39 ± 0.04</td>
<td>124.0 ± 0.2</td>
</tr>
</tbody>
</table>

* From Ref. 8.

...concentration 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 SbCl₃ 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 (C₅H₁₂N₂S)₂TeX₄, (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 Zvonkova 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 thio carbonyl 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 C₁(₄)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

* 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.

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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 $\pi$-bond interaction in tetramethylurea due
to steric repulsion between methyl groups within the molecule.

The adduct formation between antimony pentachloride and dimethyl-
ethylenurea 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 dimethylureaurea
of changes in bond angles at the carbonyl carbon atom in the 5-membered ring
can be expected to be small as $\gamma$-butyrolactone$^{13}$ and propandiol-1,2-carbo-
nate$^{14}$ give the same enthalpy changes upon adduct formation as the corre-
sponding open chain compounds.$^7$ In the sym-dimethyurea adduct one hydro-
gen 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 dimethylenurea 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 dimethylurea adduct the steric effect may be,
to a small extent, in operation.

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ylurea sample is gratefully acknowledged.

REFERENCES

1. Sutton, L. E. Tables of Interatomic Distances and Configuration in Molecules and
   388.
3. Thermal Analysis Newsletter, Perkin-Elmer Corp., Norwalk, Conn., Nos. 5 and 6.
    547.

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