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Received September 28, 1961.

## On the Donor Strength of Amides

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It has previously been suggested<sup>1</sup> that two main effects can be predicted from a comparison of the strengths of ketones and esters as donor molecules. Accordingly the inductive effect associated with the substitution of the more electronegative methoxy group for a methyl group can be expected to reduce the donor strength, while this effect may be counteracted by the delocalization of one of the two lone pairs of electrons in the ether oxygen atom. The two effects seem to balance each other in this instance.

If the carbonyl oxygen atom in an amide acts as the donor, the same two effects can be assumed to influence the donor strengths when passing from ketones to amides. The inductive effect associated with the substitution of the  $(\text{CH}_3)_2\text{N}$  group for a  $\text{CH}_3$  group should reduce the donor strength while the delocalization of the lone pair electrons of the nitrogen atom should exert an opposing influence. In order to estimate the magnitude of the donor strength of amides compared with that of ketones, some reactions between tertiary amides and acetone as donors and  $\text{SbCl}_5$  or  $\text{SnCl}_4$  as acceptors have been studied by qualitative thermochemical measurements. The effect of further substitution leading to tetramethylurea was also studied.

*Experimental.* All chemicals used were commercial products which were further purified by distillation.

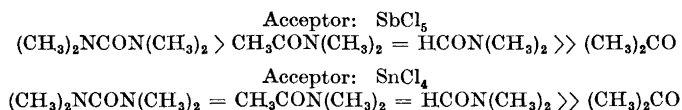
The thermochemical measurements were made in ethylene chloride solutions as described earlier<sup>2</sup>, but with different concentrations.

*Results and discussion.* In each case the infrared spectra of the addition compounds formed in the systems studied (unpublished) show a decrease in the carbonyl bond frequency (in the free molecules situated in the range 1690–1650  $\text{cm}^{-1}$ ). In the compound formed between  $\text{SbCl}_5$  and NN-dimethylformamide, however, this decrease is not significant, whereas in the compound formed with NN-dimethylacetamide the decrease is about 20  $\text{cm}^{-1}$ . A decrease in the carbonyl bond frequency was earlier assumed to indicate that the carbonyl oxygen atom functioned as the donor. Although the negligible shift found in NN-dimethylformamide cannot be explained without further investigation, there is no prior reason to suspect that this compound would react differently from NN-dimethylacetamide. From the infrared spectra, therefore, it appears as though the carbonyl oxygen atom acts as the donor in all these molecules. It is further suggested that the oxygen atom in these amides functions as a donor in compounds formed with  $\text{BCl}_3$  and  $\text{BBr}_3$ <sup>4</sup> and with  $\text{TiCl}_4$ <sup>5</sup>.

The results from the thermochemical measurements are given in Table 1. From this table it appears that the amides are much better donor molecules than the ketone. If the inductive and the delocalization effects are the main influences on the relative donor strengths when passing from ketones to amides, the delocalization effects seems to be much more significant. With  $\text{SbCl}_5$  tetramethylurea is a better donor than the amides. Other effects that can influence the donor strength cannot be excluded, but a discussion of these possible influences can only be made after further investigations of the compounds formed. In this connection a structure determination of the compound  $\text{SbCl}_5 \cdot \text{HCON}(\text{CH}_3)_2$  using X-ray techniques has already been started at this institute.

A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

Table 1.



I wish to thank Dr. I. Lindqvist for suggesting the problem and for his stimulating interest during the work and also Prof. G. Hägg for all the facilities placed at my disposal.

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Received November 1, 1961.

## A Comparison between Oxygen and Sulphur as Donor Atoms

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In an earlier paper<sup>1</sup> it was reported that ethyl sulphide has better donor properties than ethyl ether in reactions with  $\text{SbCl}_5$  and  $\text{SnCl}_4$ . It is of interest, therefore, to know whether, in comparable compounds, sulphur is always a better donor atom than oxygen in reactions with these acceptor molecules. To obtain the relevant information a few acceptor-donor reactions have been studied by qualitative thermochemical measurements. In these reactions,  $\text{SbCl}_5$  and  $\text{SnCl}_4$  were used as acceptor molecules, while comparable compounds of sulphur and oxygen comprised the donor molecules. The various donor molecules studied include different ways of bonding the donor atoms.

*Experimental.* NN-dimethyl-thioacetamide was prepared according to Kindler<sup>2</sup>. M.p. 73–74°. Other chemicals used were commercial products which were further purified by distillation.

Table 1.

Acceptor: $\text{SbCl}_5$
$\text{C}_4\text{H}_8\text{S} > \text{C}_4\text{H}_8\text{O}$
$\text{POCl}_3 \gg \text{PSCl}_3$
Acceptor: $\text{SnCl}_4$
$\text{C}_4\text{H}_8\text{S} > \text{C}_4\text{H}_8\text{O}$
$\text{CH}_3\text{CON}(\text{CH}_3)_2 = \text{CH}_3\text{CSN}(\text{CH}_3)_2$
$\text{POCl}_3 > \text{PSCl}_3$

*Acta Chem. Scand.* **15** (1961) No. 8

The thermochemical experiments were made in ethylene chloride solutions as described earlier<sup>1</sup>, but with different concentrations.

*Results and discussion.* The relative donor strengths are given in Table 1. As might be expected, tetrahydrothiophene and tetrahydrofuran show the same relative donor strengths as the ether and sulphide investigated earlier<sup>1</sup>.

In both the amide and the thioamide studied here, the molecules contain two possible donor atoms since the nitrogen atom may also have donor properties. The infrared spectra of the addition compounds show, however, that the C=O bond frequency of the amide ( $1660 \text{ cm}^{-1}$ ) decreases upon adduct formation, as does the C=S bond frequency of the thioamide ( $1280 \text{ cm}^{-1}$ ) (unpublished results). Negative shifts in the carbonyl bond frequency were earlier assumed to indicate that the carbonyl oxygen functioned as the donor<sup>3</sup>. Accordingly it appears that the oxygen atom of the amide and the sulphur atom of the thioamide are the donor atoms. The addition compound formed between NN-dimethyl-thioacetamide and  $\text{SbCl}_5$  is so slightly soluble in ethylene chloride that no measurements could be made. The adduct formed with  $\text{SnCl}_4$  also precipitates when the molar ratio, acceptor:donor, is 1:2. However, at the molar ratio 1:1, measurements could be made. The table shows that no difference in the donor strengths could be detected.

$\text{POCl}_3$  is a better donor molecule than  $\text{PSCl}_3$  and the difference is most marked when  $\text{SbCl}_5$  is used as acceptor.

From the above considerations it is impossible to state that one type of atom, oxygen or sulphur, is a better donor than the other in reactions with the acceptor molecules studied. As far as these few experiments can show, the type of bonding to the donor atom is of importance to the relative donor strengths of sulphur and oxygen. At present, however, it is not possible to explain why in molecules of the ether type sulphur is a better donor atom than oxygen, why in molecules where the donor atoms are of the carbonyl type the donor strengths of oxygen and sulphur are approximately equal, and why in phosphoryl type molecules the phosphoryl oxygen is a better donor atom than sulphur in the same position.

A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.