

## On Relative Donor Strengths: A Thermochemical Study

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A simple method for qualitative studies of relative orders of enthalpy changes has been developed. The relative orders of donor strength of some oxide chlorides and organometalloid oxides have been established. A brief discussion of the effects of substitution has been given.

In a previous paper<sup>1</sup> it has been pointed out that in the study of addition compounds, the determination of the relative acceptor and donor strengths of the reacting molecules is a very important problem. In the work described there, a spectroscopic method was used for this purpose. A more direct method is to measure the heat of reaction of the adduct formation. The discussion in the earlier paper<sup>1</sup> about such reactions in a solvent is valid in this case too.

This paper deals with an attempt to determine the relative donor strengths of a number of molecules in reactions with  $\text{SbCl}_5$  and  $\text{SnCl}_4$  as acceptors by a simple thermochemical method. In most of the reactions studied here the formation of adduct molecules is probably complete but some dissociation will not influence the measured order of donor strengths because only reactions of the same type have been compared.

### EXPERIMENTAL

*Chemicals.* 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $(\text{CH}_3)_2\text{SO}$ ,  $(\text{C}_6\text{H}_5)_2\text{S}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CH}_2\text{COOC}_2\text{H}_5$ ,  $(\text{C}_2\text{H}_5)_2\text{CO}$ ,  $(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{POCl}_3$  and  $\text{SOCl}_2$  were purified by distillation. (B.p.  $84^\circ$ ,  $95^\circ/30$  mm,  $92^\circ$ ,  $57^\circ$ ,  $77^\circ$ ,  $103^\circ$ ,  $35^\circ$ ,  $105^\circ$  and  $80^\circ\text{C}$ .)  $\text{SeOCl}_2$  was repeatedly distilled until it had a final melting point of  $+10.5^\circ\text{C}$ . In order to obtain  $(\text{C}_6\text{H}_5)_2\text{SeO}$ ,  $(\text{C}_6\text{H}_5)_2\text{Se}$  was prepared<sup>2</sup> and oxidized according to a method described by Bergson<sup>3</sup> (for preparing selenanthren-5,10-dioxide). This method gave a hydrate which was dried at  $70^\circ/10$  mm for 12 h (M.p.  $113^\circ\text{C}$ ).  $(\text{CH}_3)_3\text{PO}$  and  $(\text{C}_6\text{H}_5)_3\text{PO}$  were prepared as described earlier<sup>4</sup> (M.p.  $137-139^\circ$  and  $152-154^\circ\text{C}$ ).  $(\text{CH}_3)_2\text{SO}_2$  was prepared by oxidation of  $(\text{CH}_3)_2\text{SO}$  according to McAllan *et al.*<sup>5</sup> (M.p.  $108-109^\circ\text{C}$ ).  $(\text{C}_6\text{H}_5)_2\text{SO}_2$  was prepared by Dr. B. Sjöberg whose help is gratefully acknowledged (M.p.  $125^\circ\text{C}$ ).  $(\text{C}_6\text{H}_5)_3\text{AsO}$  was friendly sent to us by Prof. S. Y. Tyree, Chapel Hill, North Carolina.  $\text{SbCl}_5$  and  $\text{SnCl}_4$  were purified according to Dodd and Robinson<sup>6</sup>.

## THERMOCHEMICAL MEASUREMENTS

The apparatus used for this purpose is very simple. In each of two reaction vessels of Dewar type, thermistors are placed, functioning as resistances in a Wheatstone bridge. Equal volumes of a solution of the acceptor molecule are placed in the reaction vessels. The bridge is balanced with a variable resistance, using a galvanometer as null indicator. Solutions of two different donor molecules are poured into each of the vessels simultaneously. If the heat of reaction is not the same in both of the reactions the galvanometer needle deflects, thus indicating which of the reactions has the larger change of enthalpy.

1,2-Dichlorethane has been used as a solvent and the solutions of the donor molecules have been 0.4 M. Because  $\text{SbCl}_5$  in most of the cases we know gives addition compounds with one donor molecule, but  $\text{SnCl}_4$  with two molecules, 0.4 M solutions of  $\text{SbCl}_5$  and 0.2 M solutions of  $\text{SnCl}_4$  and equal volumes of donor and acceptor solutions have been used for the reactions. We have assumed that if there is any difference in the heat capacity of the solutions at such dilutions, it must be so small that it cannot influence the results. (This has also been checked by experiments which will not be presented in this paper, because only crude qualitative experiments are described here, which cannot be influenced by such minor sources of error.)

## RESULTS

The results are summarized in Table 1.

Table 1.

Acceptor:  $\text{SbCl}_5$

1.  $(\text{C}_6\text{H}_5)_2\text{SeO} = (\text{C}_6\text{H}_5)_3\text{AsO} > (\text{CH}_3)_2\text{PO} > (\text{CH}_3)_2\text{SO}$
2.  $(\text{C}_2\text{H}_5)_2\text{S} > (\text{CH}_3)_2\text{CO} = \text{CH}_3\text{COOC}_2\text{H}_5 = (\text{C}_2\text{H}_5)_2\text{CO} = (\text{C}_2\text{H}_5)_2\text{O}$
3.  $(\text{CH}_3)_2\text{SO}_2 > (\text{C}_6\text{H}_5)_2\text{SO}_2 = \text{POCl}_3 = \text{SeOCl}_2 > \text{SOCl}_2$

Acceptor:  $\text{SnCl}_4$

1.  $(\text{C}_6\text{H}_5)_2\text{SeO} = (\text{C}_6\text{H}_5)_3\text{AsO} > (\text{CH}_3)_2\text{PO} > (\text{C}_6\text{H}_5)_2\text{PO}$
2.  $(\text{C}_2\text{H}_5)_2\text{S} > (\text{CH}_3)_2\text{CO} = \text{CH}_3\text{COOC}_2\text{H}_5 > (\text{C}_2\text{H}_5)_2\text{CO} = (\text{C}_2\text{H}_5)_2\text{O}$

The donor molecules studied fall naturally into three classes of decreasing strength. Each of the compounds of a class are of the same order of strength compared to the difference between the classes, which is especially large between class 1 and class 2. The sequence within each class is not definitely proved to be correct but the experiments strongly indicate the given order. Such a small amount of substance of  $(\text{C}_6\text{H}_5)_3\text{AsO}$  was available that solutions which were only 0.04 M had to be used. The effect at this dilution is very small and the position of this donor in the sequence is thus doubtful, but its placement in class 1 is certainly correct.

$(\text{C}_6\text{H}_5)_3\text{PO}$  gives  $\text{HCl}$ -evolution and dark color with  $\text{SbCl}_5^4$  even at this dilution and could not be studied with that acceptor.  $(\text{CH}_3)_2\text{SO}$  could not

be studied with  $\text{SnCl}_4$  as acceptor because of the formation of a precipitate. The nature of this precipitate was not further explored. The compounds of class 3 gave no measurable effect with  $\text{SnCl}_4$  as acceptor. The reason is probably that the addition compounds are completely dissociated in their components at this dilution.

#### DISCUSSION

It is often assumed that the order of relative donor strengths of the molecules will also give information about the bond strength between the donor and the acceptor atoms of the compound formed. There are some objections against this assumption, however. In adduct formation the acceptor molecule has changed its structure completely and there might be subsequent energy changes which have been ignored in the assumption. For the determination of *relative* interaction strengths with the same acceptor molecule this complication is of importance only if the structure of the donor molecule also has changed appreciably.

Another complication is the fact that in some cases a secondary acceptor-donor interaction takes place, *e.g.* with  $\text{SeOCl}_2$ <sup>7</sup> and with sulfoxides<sup>8</sup>. In the detailed discussion of the order of relative donor strengths this secondary interaction might be important.

Finally it can be remarked that any attempt to subdivide the energy of a molecule into different bond energies is a rather arbitrary procedure.

The donor function of the oxygen atoms in  $\text{POCl}_3$ <sup>9</sup>,  $(\text{C}_6\text{H}_5)_2\text{SO}$ <sup>8</sup>,  $(\text{CH}_3)_3\text{PO}$ <sup>10</sup>, and  $(\text{C}_6\text{H}_5)_2\text{SO}_2$ <sup>11</sup> with  $\text{SbCl}_5$  as acceptor and in  $\text{POCl}_3$ <sup>10</sup> and  $\text{SeOCl}_2$ <sup>7</sup> with  $\text{SnCl}_4$  as acceptor has recently been definitely established by X-ray work and there is no reason to suspect that the other molecules studied here, in which oxygen is bonded to the central atom of the molecule, will react differently. Concerning the ether and the sulfide it can safely be assumed that the oxygen and the sulfur atoms, respectively, are the donor atoms. In ethyl acetate it is not established which of the oxygen atoms functions as the donor atom and it should be of great interest to know.

The results show that not only the donor atom, but also the other atoms in the donor molecule are of great importance for the donor strength. All oxychlorides are much weaker as donors than the corresponding compounds with organic substituents. The larger electronegativity of chlorine compared with the organic groups causes a drift of electrons from oxygen and thus a lower tendency to donate an electron pair. In most cases we can even see the difference between molecules with the same central atom but with different organic substituents.

Other facts also seem to influence the donor strength. Sulfur in  $(\text{CH}_3)_2\text{SO}$  and carbon in  $(\text{CH}_3)_2\text{CO}$  have the same electronegativity (2.5). Nevertheless,  $(\text{CH}_3)_2\text{SO}$  has much stronger donor properties than  $(\text{CH}_3)_2\text{CO}$ . One difference between those molecules is that the sulfur atom of the sulfoxide has a free electron pair lacking at the carbon atom in acetone.

In class 2 we can note that ethyl sulfide seems to be a stronger donor than ethyl ether. Ahrlund *et al.*<sup>12</sup> have divided acceptor atoms into two classes and placed antimony and tin in the class which should form more stable

complexes with oxygen than with sulfur, but these experiments indicate that they are probably border-line elements.

It has been established that only one of the oxygen atoms in the sulfones is functioning as a donor atom<sup>11</sup> and the other oxygen atom seems to decrease the donor strength to an appreciable extent compared with methyl-sulfoxide.

Steric hindrances might also affect the strength of the acceptor-donor bond, but there is no obvious example of this among the molecules studied.

These experiments give good hope of further exploring relative donor and acceptor strengths in a simple way. We also intend to improve the apparatus and perhaps be able to give an approximative value of the magnitude of the enthalpy changes at the reactions.

A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged. Finally we wish to thank Prof. G. Hägg for all facilities put at our disposal.

#### REFERENCES

1. Kinell, P.-O., Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **13** (1959) 190.
2. *Organic synthesis* Coll. Vol. II (1943) 238.
3. Bergson, G. *Acta Chem. Scand.* **11** (1957) 580.
4. Lindqvist, I. and Olofsson, G. *Acta Chem. Scand.* **11** (1959) 1753.
5. McAllan, D. T., Cullum, T. V., Dean, R. A. and Fidler, F. A. *J. Am. Chem. Soc.* **73** (1951) 3627.
6. Dodd, R. E. and Robinson, P. L. *Experimental Inorganic Chemistry*, Amsterdam 1954, p. 210, 216.
7. Hermodsson, Y. *To be published.*
8. Hansson, A. and Vänngård, M. *To be published.*
9. Lindqvist, I. and Brändén, C.-I. *Acta Cryst.* **12** (1959) 642.
10. Brändén, C. I., and Lindqvist, I. *To be published.*
11. Hansson, A. *To be published.*
12. Ahrland, S., Chatt, J. and Davies, N. R. *Quart. Revs.* **12** (1958) 265.

Received October 24, 1959.