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Solvent Effect on the Efficiency of Donor–Acceptor Interaction

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Abstract—Heats of solution and enthalpies of donor–acceptor interaction of several organic O-bases with $SbCl_5$ in dichloroethane, benzene, nitrobenzene, butyl acetate, and acetone were determined by calorimetry. The correlation between the interaction enthalpies and the donor number of O-base is linear in all the solvents. The structure of an inert solvent does not affect the slope of the dependences and is manifested in mutual arrangement of the curves, with the shift being proportional to the donor number of the solvent.

The prediction of the reactivity of substances in nonaqueous media gains increasing importance owing to wide development of nonaqueous (solvometallurgical) methods for processing raw materials of nonferrous, rare, and radioactive elements [1]. As applied to extractive leaching, concentration, and separation of elements, this problem consists in the development of methods for quantitatively characterizing the reactivity of components in donor–acceptor interactions on which these processes are based.

Donor or acceptor properties of substances are most often characterized by the enthalpies of donor–acceptor reactions (1) between acceptors **A** and donors **B**, which should be carried out under comparable conditions.

$$\mathbf{A} + \mathbf{B} = \mathbf{AB}. \qquad (1)$$

The major problem in this case is the selection of standard experimental conditions. An ideal medium for the comparison of properties of the donors is the gas phase [2]. However, until recently it was possible to study only a few Lewis acid–base reactions in this medium. The majority of compounds of interest cannot be transferred into a gas phase at all. The study of donor–acceptor reactions in condensed phases is complicated by solvation effects, which can completely invert the trends in variation of donor and acceptor properties of components relative to the gas phase.

Inert solvents fairly well approximate the gas phase in this respect [3]. In this case, a solvent is considered inert if it is incapable of specific interactions with participants of a donor–acceptor reaction and if its solvation interactions with acceptor **A** and donor **B** are less strong than donor–acceptor interactions in the reaction product **AB**. However, specifically the inertness of such solvents (and hence their poor solvency) is the factor limiting their application. For example, among products of Lewis acid–base reactions, only adducts of tin, titanium, and gallium chlorides can be dissolved and, therefore, studied in inert solvents.

When using solvents with a higher solvency, it is necessary to know and to take into account additional contributions resulting from solvation of all the reaction participants (**A**, **B**, and **AB**).

Overcoming these difficulties is connected with studying displacement reactions (2).

$$\mathbf{AB}_{1(S)} + \mathbf{B}_{2(S)} \rightleftarrows \mathbf{AB}_{2(S)} + \mathbf{B}_{1(S)}, \quad \Delta H_{(1)}. \qquad (2)$$

Here **A** is a Lewis acid, $\mathbf{B}_1$ and $\mathbf{B}_2$ are bases, and the index (S) indicates that the reaction occurs in a polar solvent.

Let us assume that the main energy factor in solvation will be determined by the effect of the primary solvation. The adducts $\mathbf{AB}_{1(S)}$ and $\mathbf{AB}_{2(S)}$ are coordination-saturated, and the energy of their interaction with a solvent will be determined by secondary solvation (a small contribution of formation of van der Waals bonds, resizing of voids, etc.).

It follows from [4–6] that, if the interaction of adducts $\mathbf{AB}_1$ and $\mathbf{AB}_2$ and bases $\mathbf{B}_1$ and $\mathbf{B}_2$ with a solvent S is nonspecific (i.e., no H bonds are formed and the interaction products do not dissociate), the thermal effects of solvation of the initial and final compounds should compensate each other. Naturally, this suggests

Table 1. Enthalpies of the reactions of $SbCl_5$ with O-bases **VI**–**IX** and **XI**–**XVI**[a] in organic solvents **I**–**V**

Base	$-\Delta H(SbCl_5–\mathbf{B}_i)_{(S)}$, kcal mol^{-1}				
	I	**II**	**III**	**IV**	**V**
VI	20.01 ± 0.18	18.73 ± 1.3	13.60 ± 0.12	1.46 ± 0.23	
VII	23.62 ± 0.22	21.30 ± 1.4		7.53 ± 0.17	1.17 ± 0.08
VIII	29.81 ± 0.41		21.72 ± 0.07	10.63 ± 1.13	1.65 ± 0.12
XIII	30.32 ± 0.58				1.27 ± 0.09
IX	31.22 ± 0.06			13.13 ± 0.48	2.15 ± 0.13
XIV	33.81 ± 0.06	30.82 ± 1.4	24.61 ± 0.15	15.52 ± 0.32	4.82 ± 0.12
XII	34.04 ± 0.16	30.76 ± 0.13	26.80 ± 0.16		3.01 ± 0.15
XI	38.81 ± 0.08	Insoluble	29.63 ± 0.09	16.72 ± 0.66	7.44 ± 0.20
XV	44.85 ± 0.21			22.62 ± 0.37	14.18 ± 0.16
XVI	52.32 ± 1.42			32.30 ± 0.29	16.69 ± 0.42

[a] Bases are given in the order of increasing donor number.

that the reactions of **A** with **B** and S are similar and equilibrium (3) is completely shifted toward formation of the reaction products.

$$\mathbf{A}S_{(S)} + \mathbf{B}_{i\,(S)} \rightleftarrows \mathbf{AB}_{i\,(S)} + S_{(S)}. \qquad (3)$$

Here the solvent exhibits donor properties and is incapable of specific interaction with **A**, **B**, and **AB**; by definition, such solvents are classed with indifferent solvents [7]. In this case, the enthalpies of reaction (2) obtained in inert and indifferent solvents should coincide.

Then, if the enthalpy of donor–acceptor reaction (4) of a standard acceptor in an inert solvent (dichloroethane and carbon tetrachloride) with a certain donor $\mathbf{B}_1$ is known, the sum $\Delta H_{(1)} + \Delta H_{(2)}$ will give $\Delta H_{(3)}$ of reaction (5) with any other donor $\mathbf{B}_i$.

$$\mathbf{A}(CCl_4) + \mathbf{B}_1(CCl_4) = \mathbf{AB}_1(CCl_4), \quad \Delta H_{(2)}, \qquad (4)$$

$$\mathbf{A}(CCl_4) + \mathbf{B}_i(CCl_4) = \mathbf{AB}_i(CCl_4), \quad \Delta H_{(3)}. \qquad (5)$$

On this basis, a scale of donor properties of organic bases is constructed.

Using a thermodynamic cycle, we can readily show that the enthalpy of reaction (6) is described by Eq. (7).

$$\mathbf{A}_{(S)} + \mathbf{B}_{i\,(S)} = \mathbf{AB}_{i\,(S)}, \qquad (6)$$

$$\Delta H(\mathbf{A}–\mathbf{B}_i)_{(S)} = \Delta H(\mathbf{A}–\mathbf{B}_i)_{CCl_4} + \Delta H_{tr}(\mathbf{AB}_i) - \Delta H_{tr}(\mathbf{A}) - \Delta H_{tr}(\mathbf{B}_i). \qquad (7)$$

Here $\Delta H(\mathbf{A}–\mathbf{B}_i)_{(S)}$ is the enthalpy of the donor–acceptor reaction of a standard acceptor **A** with a base $\mathbf{B}_i$ in a solvent S; $\Delta H_{tr}(\mathbf{AB}_i)$, $\Delta H_{tr}(\mathbf{A})$, and $\Delta H_{tr}(\mathbf{B}_i)$ are the enthalpies of transfer of $\mathbf{AB}_i$, **A**, and $\mathbf{B}_i$ from the solvent S into CCl_4. For the standard acceptor $SbCl_5$, $\Delta H(\mathbf{A}–\mathbf{B}_i)_{CCl_4}$ is equal to Gutmann's donor number by definition [8]. The variation of $\Delta H(\mathbf{A}–\mathbf{B}_i)_{(S)}$ in a series of $\mathbf{B}_i$ (i = 1, 2, ..., n) in polar indifferent solvents should be determined only by the donor number of the base; the values of $\Delta H_{tr}(\mathbf{AB}_i)$ and $\Delta H_{tr}(\mathbf{B}_i)$ compensate each other. In this work, we tested this concept.

We used the following solvents (in order of increasing donor numbers): dichloroethane (**I**), benzene (**II**), nitrobenzene (**III**), butyl acetate (**IV**), and acetone (**V**). As O-bases we used tetrahydrofuran (**VI**), tributyl phosphate (**VII**), dimethyl sulfoxide (**VIII**), diisoamyl (**IX**) or dioctyl (**X**) methyl phosphonate, hexamethylphosphoramide (**XI**), pyridine oxide (**XII**), dioctyl sulfoxide (**XIII**), trioctylphosphine oxide (**XIV**), dioctoxyphenyl selenoxide (**XV**), and trioctylamine oxide (**XVI**). The experimental data are given in Tables 1 and 2.

It is evident from Table 1 that the reactions of $SbCl_5$ with organic O-bases in all solvents become more exothermic with increasing donor number of the base.

This dependence is shown graphically in the figure. It is seen that the points describing donor–acceptor interaction of $SbCl_5$ with the bases in all the solvents can be fitted by straight lines almost parallel to each other:

Table 2. Enthalpies of solution of O-bases **VI**–**IX** and **XI**–**XVI**[a] in organic solvents **I**–**V**

Base	$-\Delta H_{\mathrm{soln}}(\mathbf{B}_i)_{(\mathrm{S})}$, kcal mol^{-1}				
	I	**II**	**III**	**IV**	**V**
VI	0.41 ± 0.03	0.81 ± 0.09	0.498 ± 0.04	1.27 ± 0.09	
VII	–0.59 ± 0.06	0.39 ± 0.06		0.48 ± 0.07	1.17 ± 0.08
VIII	–0.91 ± 0.07	Insoluble	–0.60 ± 0.03	1.28 ± 0.05	–0.58 ± 0.09
XIII	–13.0 ± 0.01				–14.26 ± 0.12
IX	3.44 ± 0.16			0.17 ± 0.06	–2.34 ± 0.30
XIV	–14.00 ± 0.23	–12.1 ± 0.40	–13.6 ± 0.25	–12.66 ± 0.6	–15.95 ± 0.20
XII	–2.67 ± 0.13	–0.67 ± 0.05	–0.48 ± 0.04		3.39 ± 0.19
XI		Insoluble	1.20 ± 0.08	0.94 ± 0.13	0.37 ± 0.04
XV	–13.27 ± 0.33			–13.77 ± 0.12	–11.45 ± 0.4
XVI	–7.97 ± 0.31			–11.04 ± 0.09	–13.63 ± 0.60

[a] Bases are given in the order of increasing donor number.

$$\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathrm{S})} = aDN + b. \qquad (8)$$

The least-squares treatment of the experimental data for the linear portions of the plots gave Eqs. (9)–(12) for the correlations of $\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathrm{S})}$ with DN in solvents **II**–**V**:

$$\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathbf{II})} = (0.85 \pm 0.03)DN + 1.41 \pm 0.74; \quad R\ 0.998, \qquad (9)$$

$$\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathbf{III})} = (0.86 \pm 0.06)DN - 3.67 \pm 1.91; \quad R\ 0.992, \qquad (10)$$

$$\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathbf{IV})} = (0.87 \pm 0.06)DN - 14.80 \pm 2.08; \quad R\ 0.985, \qquad (11)$$

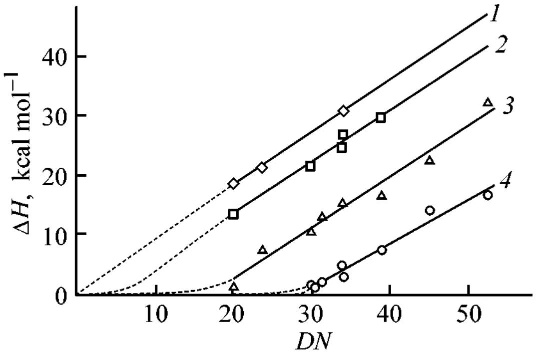
$$\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathbf{V})} = (0.73 \pm 0.05)DN - 20.65 \pm 1.97; \quad R\ 0.985. \qquad (12)$$

The coefficients of the equations show that the linear portions of the curves have almost the same slope; the solvent effect on the enthalpy of donor–acceptor reactions is manifested only in the constant b. However, Eq. (8) characterizes only a part of the overall dependence. As seen from the figure, it is a complicated curve consisting of three parts: the first part with $\Delta H(\mathrm{SbCl_5}-\mathbf{B}_i)_{(\mathrm{S})}$ close or equal to zero, the second transition part, and the third part described by Eq. (8).

Changing a solvent changes not the curve shape, but only its position in the selected coordinate system. In fact, the shift of the curves along the abscissa reflects the transfer of a donor–acceptor reaction of $\mathrm{SbCl_5}$ with an O-base from one solvent into another. As shown earlier, this trend can be described by Eq. (13).

$$\Delta H(\mathbf{A}-\mathbf{B}_i)_{(\mathrm{S})} = DN + \Delta H_{\mathrm{tr}}(\mathbf{AB}_i) - \Delta H_{\mathrm{tr}}(\mathbf{A}) - \Delta H_{\mathrm{tr}}(\mathbf{B}_i). \qquad (13)$$

According to the assumption made, $\Delta H_{\mathrm{tr}}(\mathbf{AB}_i) - \Delta H_{\mathrm{tr}}(\mathbf{B}_i) \approx 0$, and $\Delta H_{\mathrm{tr}}(\mathrm{SbCl_5})$ is determined by the energy of resolvation of antimony pentachloride and should approach the solvent donor number. These considerations are supported by the following experimental data. The terms b in the equations for solvents **III**–**V** are close to the donor numbers for these solvents: **III**, 3.64 (DN 4.4); **IV**, 16.8 (DN 17.0); and **V**, 20.2 (DN 17.0). The deviation of the value for acetone seems to result from reversible processes of



Correlation of the enthalpy of reaction of $\mathrm{SbCl_5}$ with O-bases in various organic solvents with the donor number of the base: (*1*) benzene, (*2*) nitrobenzene, (*3*) butyl acetate, and (*4*) acetone.

dissociation–association of antimony pentachloride in this solvent.

The data obtained confirm our assumptions concerning the solvent effect on the efficiency of donor–acceptor reactions and open up a possibility for using indifferent solvents to obtain comparable thermodynamic characteristics of the donor power for a wide range of compounds which cannot be studied in inert solvents.

EXPERIMENTAL

To obtain quantitative characteristics of the donor power of organic O-bases and also to study the solvent effect on the efficiency of donor–acceptor reactions, we have measured the heat effects of reaction (14).

$$\mathrm{SbCl}_{5(\mathrm{S})} + \mathbf{B}_i = \mathrm{SbCl}_5\text{–}\mathbf{B}_{i\,(\mathrm{S})},\ \Delta H(\mathrm{SbCl}_5\text{–}\mathbf{B}_{i\,(\mathrm{S})}). \quad (14)$$

These measurements were made by Gutmann's technique [8]. Weighed portions of bases (in total, no more than 2–4 mmol) in 25 ml of a solvent were added sequentially to a tenfold excess of SbCl_5 (4–12 mmol).

The enthalpy of reaction (14) was calculated by formula (15).

$$\Delta H(\mathrm{SbCl}_5\text{–}\mathbf{B}_i)_{(\mathrm{S})} = Q - \Delta H_{\mathrm{dis}}(\mathbf{B}_i)_{(\mathrm{S})}. \quad (15)$$

Here Q is the thermal effect of the process determined by Gutmann's technique, and $\Delta H_{\mathrm{dis}}(\mathbf{B}_i)_{(\mathrm{S})}$ is the enthalpy of solution of a base $\mathbf{B}_i$ in a solvent S. These values were determined by a similar technique, but in the absence of SbCl_5 (Table 2).

The solvents were purified and dried by the standard technique [9]; the water content in the solvents, determined by Fischer titration, did not exceed 0.005%. We failed to dehydrate solvent **V** completely. Prior to thermochemical experiments, acetone was specially dehydrated by neutralization of excess water with a certain amount of antimony pentachloride. Compounds **VII**–**XI** were purified by fractional distillation and dehydrated in a high vacuum over $\mathrm{P_2O_5}$. Compounds **XII**–**XVI** were purified by repeated recrystallization from appropriate solvents and dehydrated by freezing in a high vacuum. The water content in compounds **XII**–**XIV** did not exceed 0.01%, and that in compounds **XV** and **XVI**, 0.02–0.03%.

The measurements were carried out under isothermal conditions at 25°C using a modified Vorob'ev–Skuratov calorimeter. The sensitivity of the measuring system to temperature variation was 5×10^{-5} K; the accuracy of temperature control, 0.01 K; and the reproducibility of the thermal number of the calorimeter, ±0.15%. Hermetic sealing of the calorimeter was provided by Teflon gaskets and silphon fittings on the stirrer drive shaft. In experiments with acetone, we used a semi-sealed calorimetric cell (contact to air medium through a packing gland). The total error of the electrical and current measurements was 1.08%; the total relative error of the thermochemical experiments did not exceed 2–3%.

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