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CALORIMETRIC STUDIES IN SOLUTION. I. INFLUENCE OF THE SOLVENT ON THE RELATIVE STANDARD ENTHALPY OF STEREOISOMERS

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If we consider an $A \rightleftharpoons B$ equilibrium, the thermodynamic parameters (K, ΔG°, ΔH°, ΔS°) which characterize this equilibrium are solvent dependent if, as usually, the equilibrium constant K is defined by the concentrations ratio (B)/(A) (1).

Therefore, the thermodynamic parameters measured in a solvent S can be described as the sum of an intramolecular and an intermolecular contributions. So, for the standard enthalpy, we have :

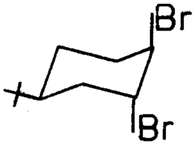
$$(\Delta H°)_S = \Delta H°_{intra} + (\Delta H°_{inter})_S$$

We shall define cyclohexane as the reference solvent, S_1, and $(\delta\Delta H°)^{S_1}_{S_2}$ as the variation of the standard enthalpy when the A/B system is transfered from the reference solvent cyclohexane to the solvent S_2. We have thus :

$$(\delta\Delta H°)^{S_1}_{S_2} = (\Delta H°_{inter})_{S_2} - (\Delta H°_{inter})_{S_1}$$

The $I_{aa} \rightleftharpoons I_{ee}$ equilibrium of trans 1,2-dibromocyclohexane (I) is solvent dependent and this system has been used by Abraham and Sievers (2) to test the Abraham's solvent effect theory (3). We have investigated a closely related system by solution calorimetry.

Using II and III as solutes, we have measured $(\Delta\delta H°)^{S_1}_{S_2}$ for various solvents. It must be observed that $(\Delta\delta H°)^{S_1}_{S_2} = (\delta\Delta H°)^{S_1}_{S_2}$ since the operators δ and Δ are commutable (1).



II

III

The pure liquid II (∿ 0,5 g) is dissolved in a large excess (∿ 100 ml) of cyclohexane and the conditions of infinite dilution are considered to be performed. The dissolution heat effect, $Q_{S_1}^{II}$ is measured.

The corresponding molar enthalpy is then calculated taking into account the number, $n_{S_1}^{II}$, of moles of II in the solution

$$\Delta H_{S_1}^{II} = \frac{Q_{S_1}^{II}}{n_{S_1}^{II}}$$

In successive experiments, $\Delta H_{S_2}^{II}$, $\Delta H_{S_1}^{III}$ and $\Delta H_{S_2}^{III}$ are similarly measured.

Each of these values, in itself, is a difference between, on the one hand, the auto solvation enthalpy of the pure liquid and, on the other hand :

1°) the solvation enthalpy (enthalpy associated with the solvent-solute interactions) and

2°) the enthalpy associated with the cage formation in the solvent.

The differences $(\Delta H_{S_2}^{II} - \Delta H_{S_1}^{II})$ or $(\Delta H_{S_2}^{III} - \Delta H_{S_1}^{III})$ are evidently independant of the auto solvation energy.

More generally, therefore the value of $(\Delta\delta H°)_{S_2}^{S_1}$ given by the following equation :

$$(\Delta\delta H°)_{S_2}^{S_1} = (\Delta H_{S_2}^{III} - \Delta H_{S_1}^{III}) - (\Delta H_{S_2}^{II} - \Delta H_{S_1}^{II})$$

is only a function of : 1°) the enthalpy associated with the cavity formation in S_1 and S_2 (these terms are related with properties of the solvent like internal pressure (4) or viscosity (5) but also with properties of the solute i.e. molecular volume and shape).

2°) the energy of interaction of each stereoisomer with each solvent, S_1 and S_2.

Table I gives some values of $(\Delta\delta H°)_{S_2}^{S_1}$ obtained in various solvents.

Table I : $(\Delta\delta H°)_{S_2}^{S_1}$ between III and II (in kcal/mole). Error : ± 40 cal/mole.

(measurements were made at 25°C on a LKB 8700 calorimeter (S_1 = cyclohexane))

Solvent	cyclohexane	CCl_4	CS_2	C_6H_6	acetone
$(\Delta\delta H°)_{S_2}^{S_1}$	0,00	- 0,15	- 0,43	- 1,33	- 1,36

Compared to the less polar stereoisomer II, the polar stereoisomer III is stabilized in CCl_4, CS_2, C_6H_6 and acetone if we take cyclohexane as reference solvent.

This general behaviour is normal if we consider the higher polarisability or polarity (in the case of acetone) of these four solvents compared to cyclohexane. Nevertheless, the solvents sequence cannot be explained only on the basis of an effect like the reaction field of the solvent. The energy associated with the cavity formation seems to play an important role together with the London's and Debye's solvent-solute interaction energy terms.

The "abnormal" behaviour of C_6H_6, acting as solvent, is frequently observed (2,6). Table I gives a quantitative measure of this "abnormality". It must be said that benzene is abnormal if it is compared to other solvents on the basis of the dielectric constant alone (2).

The high polarisability of benzene and its flat shape certainly contribute to the solvent properties via the cavity term and the London's and Debye's interaction energies.

Our $(\Delta\delta H^\circ)_{S_2}^{S_1}$ values are not directly comparable to the $(\delta\Delta G^\circ)_{S_2}^{S_1}$ which have been determined for the $I_{aa} \rightleftharpoons I_{ee}$ system (2,7). It is not obvious that a $(\Delta\delta H^\circ)_{S_2}^{S_1}$ value measured on the II/III system is directly transferable to the I_{aa}/I_{ee} system and this problem is intimately related with the general problem of model molecules in conformational analysis. Nevertheless, the $(\delta\Delta S^\circ)_{S_2}^{S_1}$ question is in our point of view much more important. It seems difficult to imagine the existence of an intermolecular contribution to the standard enthalpy without a corresponding contribution to the standard entropy, the two contributions probably being correlated (1,8).

This problem is now under investigations.

To conclude this note, it can be said that solution calorimetry appears as an extremely powerful method for the study of the energetic aspects of the solvent-solute interactions in relations to stereochemical problems.

Experimental part

Each ΔH_S measurement were made several times. The reproductibility is of the order of ± 10 cal/mole. The well-known reaction of TRIS + HCl is used to test the instrument (9). The accuracy of the calorimetric measurement is excellent. The error on the experimental values (table I) is estimated at ± 40 cal/mole (addition of absolute errors).

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