



Determination of sublimation enthalpies of substituted benzophenones, fluorenes and diphenyl ethers by solution calorimetry approach



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ABSTRACT

An approach for the determination of solvation enthalpies of substituted aromatic compounds is developed. In this work the solvation enthalpy of a reference unit (benzophenone, fluorene and diphenyl ether) is calculated as the difference between solution enthalpy and sublimation enthalpy at 298 K. An additive approach for the determination of solvation enthalpies of substituted aromatic compounds was used. Solvation enthalpies of sixteen substituted benzophenones, fluorenes and diphenyl ethers were calculated by this approach. Thermochemical data of solution enthalpies of benzophenones, fluorenes and diphenyl ether were measured by a precision solution calorimeter at 298 K. Then sublimation enthalpies of the studied compounds were derived by a solution calorimetry (SC) approach at 298 K.

We have also found that in a number of cases instead of the solution enthalpy in benzene at 298 K the fusion enthalpy at the melting temperature can be used. A comparison between literature data and the calculated vaporization and sublimation enthalpies demonstrates a satisfactory performance of the proposed approach.

1. Introduction

Substituted benzophenones, fluorenes and diphenyl ethers are widely used in the pharmaceutical industry and perfumery. Consequently thermochemical properties of phase transitions are necessary to determine the solubility of these compounds. For example the solubility of fluorenes and benzophenones is an important property because many of its derivatives are pollutants [1,2].

However thermochemical data of these compounds are poorly studied in the literature. The enthalpies of the sublimation of some compounds haven't been derived yet. This is due to the difficulties in the determining of the sublimation enthalpy by conventional methods [3,4]. Only the sublimation enthalpies of unsubstituted benzophenone and fluorene were studied well. Eleven values of sublimation enthalpies of benzophenone and eight values for fluorenone are available in the literature. This is due to the fact that thermochemical properties of unsubstituted compounds are usually easier to study. It is related to the fact that unsubstituted compounds as a rule are more easily volatile and stable than substituted compounds. Thermochemical properties of benzophenone derivatives were studied in [5–7], fluorene derivatives in [8–12] and diphenyl ether derivatives in [13,14]. In some cases, values obtained by various authors are in disagreement (for example: 2,7-dibromofluorene [8–10]), in other cases only one value is available in the literature (for example: 4-chlorobenzophenone [6]).

In previous works [15–21] we have shown that enthalpies of sublimation at 298 K can be derived using a solution calorimetry (SC) approach. One of the most important advantage of using the SC approach is that vaporization/sublimation enthalpies are derived directly at the reference temperature (298 K) that's why the SC approach can be used for studies of thermally instable and explosive compounds. Another advantage of the SC approach appears from the well-known fact that conventional methods for measurements of phase transition enthalpies are highly sensitive to impurities. Moreover, solution calorimetry can be used for low volatile compounds [21]. In this case, only several experimental methods can be applied for these compounds [3].

According to the SC approach the vaporization and sublimation enthalpies can be calculated as the difference between the solution enthalpy of compound A_i in solvent S and solvation enthalpy in the same solvent at 298 K. The solution enthalpy can be experimentally measured by a solution calorimeter. In works [18,20,21] it was shown that solvation enthalpies can be estimated by a linear dependence of the solvation enthalpy of compound A_i and molar refraction. This approach is most universal for cyclohexane. The most multipurpose approach for the determination of solvation enthalpies of different compounds and various solvents was proposed in the works [15–17,19]. According to this approach, the solvation enthalpy is calculated as a sum of the solvation enthalpy of the reference unit and contributions due to the substitution of the hydrogen atoms in the reference unit by any other

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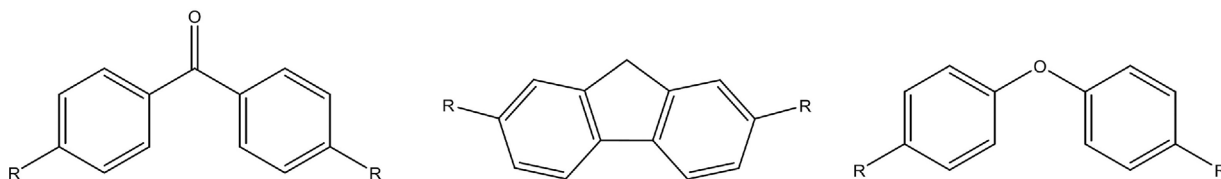


Fig. 1. Compounds studied in this work: mono and di substituted benzophenones, fluorenes and diphenyl ethers with R = OH, CH₃, OCH₃, NH₂, C(O)NH₂.

groups. In some cases solvation enthalpy of the reference unit may be calculated by an additive scheme [17]. In other cases the solvation enthalpy of the reference unit may be calculated as the difference between the solution enthalpy of solute A_i in solvent S and vaporization/sublimation enthalpy [16,19].

In this work the previously described approach [19] for the determination of solvation enthalpies is applied to substituted aromatic compounds.

2. Experimental part

2.1. Materials

All substituted and unsubstituted benzophenones, fluorenes and diphenyl ether used in this work were of a commercial origin (Fig. 1). Purity of all samples before purification was 98–99% (see Table S1). Some of the samples were additionally purified by vacuum sublimation method. Benzophenone was recrystallized from ethanol and dried under reduced pressure. Benzene was washed with H₂SO₄, NaOH, water and then distilled over CaH₂. Final mass fraction purity was determined using a gas chromatography with capillary column HP-5 with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The gas chromatograph is equipped with flame ionization detector. The water content in benzene was determined using Karl Fisher titration.

2.2. Solution calorimetry

Solution enthalpies of all studied compounds were derived by a solution calorimetry. In this work we used a precision solution calorimeter TAM III in a concentration range of 1–17 mmol kg⁻¹ at 298 K. Solid samples were dissolved by breaking a glass ampule in a glass cell containing the pure solvent. Liquid sample of diphenyl ether in benzene was dissolved using titration procedure. Small portions of solute were injected in the glass cell with 100 ml of benzene using an electronically operated syringe equipped with a long gold cannula. The details of the solution calorimetry experimental procedure have been fully described elsewhere [21].

Detailed data on the measurement of solution enthalpies of studied compounds in benzene are listed in Table S2.

Table 1

Enthalpies of solution, solvation and sublimation of substituted benzophenones and fluorenes measured in this work at 298 K (kJ mol⁻¹).

| Compound A _i | $\Delta_{\text{soln}} H^{A_i/C_6H_6}(298\text{ K})^a$ | $-\Delta_{\text{solv}} H^{A_i/C_6H_6}(298\text{ K})$ | $\Delta_{\text{cr}}^g H^{A_i}(298\text{ K})$ |
|--------------------------------|---|--|--|
| 4-methylbenzophenone (cr) | 18.35 ± 0.15 | 80.1 ± 1.0 | 98.5 ± 1.0 |
| 4-nitrobenzophenone (cr) | 26.0 ± 0.2 | 94.5 ± 1.0 | 120.5 ± 1.0 |
| 4-chlorobenzophenone (cr) | 22.5 ± 0.3 | 82.7 ± 1.0 | 105.2 ± 1.0 |
| 4,4'-dichlorobenzophenone (cr) | 24.1 ± 0.2 | 88.8 ± 1.0 | 112.9 ± 1.0 |
| 2-bromofluorene (cr) | 16.71 ± 0.06 | 76.9 ± 1.0 | 93.6 ± 1.0 |
| 2-nitrofluorene (cr) | 26.34 ± 0.15 | 86.1 ± 1.0 | 112.4 ± 1.0 |
| 2-aminofluorene (cr) | 23.41 ± 0.06 | 84.0 ± 1.0 | 107.4 ± 1.0 |
| 2,7-dibromofluorene (cr) | 23.42 ± 0.11 | 85.6 ± 1.0 | 109.0 ± 1.0 |

^a Solution enthalpy measured in this work (see Table S2). Uncertainty correspond to expanded uncertainties of the mean U (0.95 level of confidence).

3. Results and discussion

3.1. Determination of sublimation enthalpies of substituted benzophenones and fluorenes by the solution calorimetry approach

The approach for determination vaporization and sublimation enthalpy based on the relationship between vaporization/sublimation enthalpy of compound A_i, solvation and solution enthalpies of solute A_i in solvent S:

$$\Delta_{\text{cr}}^g H^{A_i} = \Delta_{\text{soln}} H^{A_i/S} - \Delta_{\text{solv}} H^{A_i/S} \quad (1)$$

The solution enthalpy can be measured experimentally while the solvation enthalpy can be calculated. In work [19] an additive scheme for calculation enthalpy of solvation was offered. According to this scheme, solvation enthalpy of solute A_i in solvent S can be calculated as a sum of solvation enthalpy of parent aromatic hydrocarbon and contributions due to the substitution of the hydrogen atoms in the reference unit by any other groups X:

$$\Delta_{\text{solv}} H^{A_i X_n/S} = \Delta_{\text{solv}} H^{A_i H_n/S} + n \cdot \Delta_{\text{solv}} H^{X \rightarrow H/S} \quad (2)$$

Where $\Delta_{\text{solv}} H^{X \rightarrow H/S}$ were calculated as a difference between the enthalpies of solvation of monosubstituted benzene and benzene. $\Delta_{\text{solv}} H^{A_i H_n/S}$ were calculated from the literature value of vaporization/sublimation enthalpy of compound A_i and the solution enthalpy of solute A_i in solvent S [19]. In the present work for the calculation of solvation enthalpies of benzophenone and fluorene literature data of sublimation enthalpies and measured values of solution enthalpies in benzene were used.

According to Eq. (1) the solvation enthalpy of benzophenone in benzene (−76.6 kJ mol⁻¹) was calculated from the value of the solution enthalpy (18.2 kJ mol⁻¹, see Table S2) and the average literature value of the sublimation enthalpy at 298 K (94.8 kJ mol⁻¹, see Table S3). By the same way the solvation enthalpy of fluorene (−68.2 kJ mol⁻¹) was calculated. The solution enthalpy of fluorene was measured in this work (19.1 kJ mol⁻¹, see Table S2). Literature values of sublimation enthalpies of fluorene were compiled in Table S4. The average sublimation enthalpy is equal to 87.3 kJ mol⁻¹.

The contribution into solvation enthalpy due to the substitution of the hydrogen atoms in the reference unit by any other groups were taken from [19]: CH₃ (−3.5 kJ mol⁻¹), NO₂ (−17.9 kJ mol⁻¹), NH₂ (−15.8 kJ mol⁻¹), Cl (−6.1 kJ mol⁻¹) and Br (−8.7 kJ mol⁻¹). Calculated according to Eq. (2) the solvation enthalpies of substituted

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