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A DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF SOME PHENOL DERIVATIVES

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Differential scanning calorimetry has been applied to derive the fusion enthalpies and entropies of series of mono and dimethylphenols, mono and dichlorophenols, and mono and dinitrophenols.

This paper reports the result of a research carried out in our laboratory on possible correlations between the enthalpies and entropies of solid-solid and solid-liquid transitions and the molecular structures [1] of some substances with a common structure and/or chemical characteristics. A previous paper [2] dealt with the entropies and enthalpies of melting and solid-solid transitions of some alkali metal salts. From these studies it was evident that the parabolic dependence of $\Delta S^t = \Delta S^t_{s,1} + \Delta S^t_{s,s}$) upon the cationic radius is a common feature of several families of alkali metal salts.

In order to investigate further the dependence of the above-mentioned quantities on the molecular structures of different classes of compounds, it seemed interesting to study the thermodynamic behaviour of substances characterized by higher structural affinity. Accordingly, this paper deals with the thermodynamic properties of some mono and disubstituted phenol derivatives in which the only variation is the relative position of the groups. The classes of isomers, chosen mainly for their low melting points, stability and the possibility of obtaining high-purity samples, are: mono- and dimethylphenols, mono- and dichlorophenols, and mono- and dinitrophenols. Significant differences between entropies and enthalpies for compounds of the same series of isomers have been demonstrated. At the same time the different series of isomers show some analogies, such as the trends of the entropy values, which are indicative of some correlations between the structure and thermodynamic parameters.

Experimental

Chemicals:

Mononitrophenols and 2-chlorophenol were FLUKA extra-pure (99%) products. The three mononitrophenols were dried under vacuum; 2-chlorophenol, which is liquid at room temperature, was used as received.

All the other compounds were FLUKA reagent grade products, and were treated as follows before use:

4-Chlorophenol: dried under vacuum

3-Chlorophenol: a deliquescent solid at room temperature, was distilled under vacuum, the fraction boiling at 333 K being collected.

2,3-Dichlorophenol: crystallized from heptane (once) and from ether (three times).

3,5-Dichlorophenol: crytsallized from heptane (three times).

2,5-Dimethylphenol: crystallized from water-ethanol (1 : 1) mixture (once) and from ether (three times).

All the other compounds, 2,4, 2,5, 2,6 and 3,4-dichlorophenols and 2,3, 2,4, 2,6, 3,4 and 3,5-dimethylphenols, were crystallized from ether (three times).

2,3-Dinitrophenol: crystallized from water and sublimed.

2,4 and 2,5-Dinitrophenols: crystallized from water (four times) and from ethanol (twice).

2,6-Dinitrophenol: crystallized from water (four times) and from a mixture (1 : 1) of ether and ethanol (twice).

3,4-Dinitrophenol: crystallized (eight times) from water.

The compound 2-chlorophenol, liquid at room temperature, was used as received.

The last crystallization was performed by dissolving each compound in a small quantity of solvent. The solution was heated to boiling point, heated with activated carbon and filtered. The compound was finally crystallized at room temperature.

3,5-Dinitrophenol was not studied because we were unable to obtain a product of satisfactory purity.

The purity of each compound was checked using the criteria normally accepted for DSC.

Thermal and calorimetric measurements

The melting point of each compound was determined using a Reichert NEOPAN hot-stage microscope, calibrated using Reichert dried standards. These melting points are in good agreement with those provided in the literature [3]. All the calorimetric measurements were performed using a Perkin–Elmer DSC-1B differential calorimeter. Samples were weighed using a Mettler M5 balance (accuracy 0.002 mg).

Peak areas were measured using a Salmoiraghi 308 planimeter. The DSC calibration was performed by the same procedure as described in Ref. [4] using In (3N), Ga (R.P.E.), Hg (RP-ACS-distilled) and deionized, six times distilled water. The enthalpy values used for the calibration are those listed in Ref. [4].

These substances and the SHA* employed provide data which (when submitted to a least-square treatment) give the following equation for the calibration

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* (SHA = sample holder assembly)

factor $K(T)$:

$$K_T(\mathrm{J/cm^2}) = 1.4038 \cdot 10^{-2} + 1.046 \cdot 10^{-2} T.$$

All samples for calibration and measurements were prepared and sealed in Al sampling pans (Ref. [5]) in a nitrogen-filled dry-box (typical relative moisture level 1 %).

Results

Table 1 lists the values of temperatures, enthalpies and entropies of fusion of the different compounds.

The relevant data for methylphenols are taken from the literature [5].

Table 1

Relevant values of the enthalpies and entropies of fusion for mono- and dichloro-, mono- and dimethyl-, and mono- and dinitrophenols

Compound	T_m, K	ΔH_m, J mol^{-1}	ΔS_m, J mol^{-1}
3-Chlorophenol	305.8	14 905 ± 218	48.74
4-Chlorophenol	316.0	14 067 ± 142	44.51
2-Chlorophenol	283.0	12 523 ± 125	44.25
2-Methylphenol	303.0	13 938	46.00
4-Methylphenol	309.0	11 887	38.47
3-Methylphenol	285.0	9 413	33.03
3-Nitrophenol	370.0	19 196 ± 197	51.88
4-Nitrophenol	387.0	18 254 ± 134	47.17
2-Nitrophenol	318.0	17 446 ± 163	54.86
2,5-Dichlorophenol	331.0	22 434 ± 251	67.78
2,6-Dichlorophenol	340.0	22 141 ± 167	65.12
2,3-Dichlorophenol	330.0	21 363 ± 209	64.74
3,4-Dichlorophenol	341.0	20 927 ± 188	61.37
3,5-Dichlorophenol	341.0	20 509 ± 167	60.14
2,4-Dichlorophenol	318.0	20 090 ± 146	63.18
2,5-Dimethylphenol	348.0	23 376 ± 176	67.17
2,3-Dimethylphenol	346.0	21 024 ± 188	60.76
2,6-Dimethylphenol	318.9	18 897 ± 146	59.26
3,4-Dimethylphenol	334.0	18 127 ± 167	54.27
3,5-Dimethylphenol	336.8	17 997 ± 167	53.38
2,4-Dimethylphenol	299.0	—	—
2,3-Dinitrophenol	417.0	26 239 ± 209	62.92
3,4-Dinitrophenol	407.0	25 376 ± 251	62.35
2,4-Dinitrophenol	388.0	24 174 ± 180	62.30
2,5-Dinitrophenol	381.0	23 730 ± 176	62.28
2,6-Dinitrophenol	336.0	19 577 ± 167	58.26
3,5-Dinitrophenol	399.1	—	—

Mono-substituted phenol derivatives

From Table 1 it is apparent that for chlorophenols and nitrophenols, the enthalpies of fusion increase in the order ortho, para and meta. The opposite trend is observed for the corresponding methylphenols. The fusion entropies of chlorophenols and methylphenols maintain the same trend, while the fusion entropies for nitrophenols increase in the order para, meta and ortho.

Figure 1 shows a complete thermal curve for the sample of *o*-chlorophenol. A solid-solid transition is observed in the curve at a temperature about 11 – 12 K lower than the melting point. Transition heat changes depend on the cooling conditions, but assume a constant value if the samples are quenched.

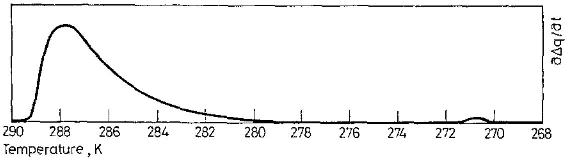

Fig. 1. DSC curve of *o*-chlorophenol; Sample weight: 6.223 mg; range: 4; scan rate: 4°/min; chart speed: 60 mm/min

The enthalpy and entropy values for the *o*-chlorophenol solid-solid transition are $\Delta H = 91.08$ J mol^{-1} and $\Delta S = 0.33$ J mol^{-1} K^{-1}.

No solid-solid transitions are observed for the other monosubstituted derivatives in Table 1 in the temperature range between 193 K and the melting points.

Disubstituted phenol derivatives

From Table 1 it is apparent that for dichloro and dimethylphenols the fusion enthalpies maintain the same trend, except for the 2,6 and 2, 3 isomers, for which the trend is reversed.

The dinitrophenol fusion enthalpies do not show any correlation of the type observed for the other two series of isomers.

2,4-Dichlorophenol excepted, all the other values reported, relative to the fusion entropy, have the same trend for the corresponding enthalpy values for all three series of isomers.

The relevant values for 2,4-dimethylphenol are not listed. This compound presents a sharp transition near 210 K; above this temperature the heating curve has the characteristic shape for a diffuse solid-solid transition ending at the melting point. This transition is present for all samples but, because of DSC-1B calibration difficulties in the lower temperature range and of the uncertain baseline, no quantitative data are reported.

No solid-solid transitions are observed for the other disubstituted compounds in the temperature range between 193 K and the melting points.

Discussion

As concerns the trend observed for the fusion entropies of the monosubstituted phenol derivatives, it is to be expected that compounds with intramolecular H bonds have a higher molar volume and fusion entropy isomers with intramolecular H bonds. This behaviour is confirmed in the case of 2-nitrophenol, which is characterized by a lower density [6] and melting point and by a higher ΔS_m value than the corresponding values for the para and meta isomers, where intermolecular H bonding is present.

Several difficulties were found in interpreting the observed fusion entropy trends for both monochloro and monomethylphenols.

Phenols also associate by H bonding, but the extent is reduced because of some, steric hindrance of the benzene ring and the formation of intramolecular H bonds particularly in the case of disubstituted phenol derivatives.

This, together with other contributions, such as the position, nature, size and orienting effects of the substituting groups, makes it difficult to rationalize the observed fusion entropy trends.

For some of the isomers studied, the literature reports thermodynamic data relative to ionization constant values (pK's) [7] which are additive. As concerns the entropy and enthalpy values reported in Table 1, only in one case may the additivity be demonstrated: the fusion enthalpy of 2,5-dimethylphenol is equal, within the experimental error, to the sum of the corresponding values for ortho and meta-methylphenols.

In the case of molecular crystals, the melting process often occurs in distinct stages, i.e., the melting point is preceded by first-order solid-solid transitions. It seems more advisable, therefore, to try to find a correlation between the molecular structure and the values of $\Delta S_{m,tr}$, rather than between the molecular structure and the values of ΔS_m [8].

For this reason the thermodynamic behaviour of all the isomers listed in Table 1 has been examined over the maximum temperature range possible with the DSC-1B (from about 193 K to the melting temperatures). A precise measure of all transition entropies (solid-solid and solid-liquid) would probably give for 2,4-dinitrophenol a value consistent with those of the other isomers.

Entropy variations determined from fusion are the resultants of two different contributions [8]: ΔS_m^V, entropy variation due to volume increase (ΔV_m), and fusion entropy at constant volume, ΔS_m^J. A greater regularity is to be expected among the ΔS_m^J data in a given group of compounds than among those relative to the simple entropy of fusion. However, the lack of density measurement data (with regard to variation of molar volumes in correspondence with transitions) prevents calculations of ΔS_m^J; only empirical correlations of the experimental entropy data (ΔS_m) may be attempted.

Correlations have been made with respect to T_m, which, for a certain isomer, may be considered to be a "structural parameter", depending on molecular and crystalline structures.

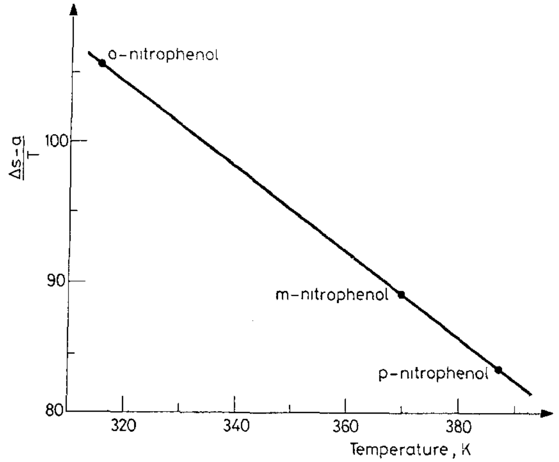

Fig. 2. Plot of $\frac{\Delta S_m - a}{T_m}$ vs. T_m for nitrophenols

For both series of mono and dichlorophenols, and mono and dimethylphenols, the attempt to correlate the fusion entropies with the temperature or with the position of the substituent has failed.

Figures 2 and 3 show the plots of ΔS_m vs. T_m, where ΔS_m is expressed as:

$$\frac{\Delta S_m - a}{T_m}$$

where a is a numerical coefficient.

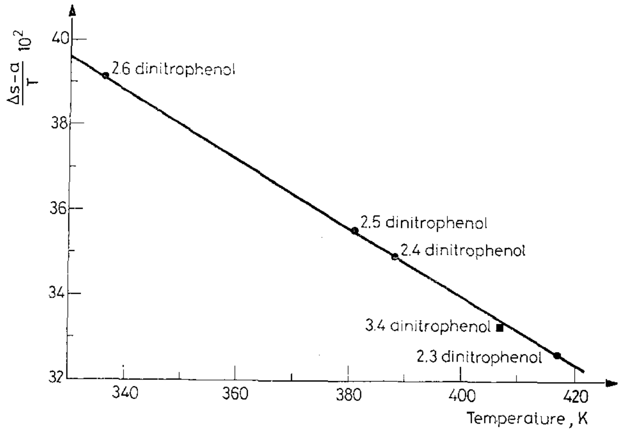

Fig. 3. Plot of $\frac{\Delta S_m - a}{T_m}$ vs. T_m for dinitrophenols

The linear plots show that the fusion entropy of mononitrophenols may be expressed by the equation:

$$\frac{\Delta S_m + 278.115653}{T_m} = 2.009465 - 3.0205 \cdot 10^{-3} T_m. \qquad (1)$$

For dinitrophenols with a $-NO_2$ group in the ortho position, the equation is:

$$\frac{\Delta S_m + 73.186488}{T_m} = 0.660388 - 0.801052 \cdot 10^{-3} T_m \qquad (2)$$

Equation (2) is also obeyed to a good approximation by 3,4-dinitrophenol.

As a concluding remark, it may be observed that, in contrast to the behaviour of mononitro derivatives, the dinitro compounds obey the Pirsch [9] effect, for which, in a series of isomers, ΔS_m increases with increasing T_m.

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ZUSAMMENFASSUNG — DSC wurde verwendet zur Ermittlung der Schmelzenthalpie und Entropie der Reihen von Mono- und Dimethylphenolen, Mono- und Dichlorphenolen, Mono- und Dinitrophenolen.

Резюме — Дифференциальная сканирующая калориметрия была использована для определения энтропии и энтальпии плавления ряда моно- и диметилфенолов, моно- и дихлорфенолов, моно- и динитрофенолов.