Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE EFFECT OF ALKYL CHAIN LENGTH ON THE THERMODYNAMIC PROPERTIES OF THE HALF ESTERS OF *o*-PHTHALIC ACID

EDWARD M. BARRALL II
IBM Research Laboratory, San José, California 95114 (U. S. A.)

(Received March 12th, 1971)

ABSTRACT

The temperature, heat and entropy of fusion of four half esters of *o*-phthalic acid have been measured. These values are compared to other aromatic acid properties on the basis of molecular weight. The calorimetric data have an accuracy of ±5% and agree well with values predicted from simple entropy, geometric and electronic considerations.

INTRODUCTION

It is generally recognized that much information concerning molecular order and arrangement may be gained from a consideration of the thermodynamic properties of a compound. The conclusions are more specific if complete data, at least temperature and entropy of fusion, are known on a series of compounds containing some regular functional change[1]. To date, complete thermal data are known for only a few homologous series. The principal reason for this condition is the difficulty of classical calorimetric analysis . In the past decades, dynamic or scanning calorimetric methods have been developed to a high degree of speed and simplicity and reasonable accuracy. Differential scanning calorimetry (DSC) is now sufficiently understood to employ the method as a tool in calorimetric analysis[2-4]. DSC is applicable to those systems in which equilibrium is rapidly attained. The ultimate precision and accuracy cannot equal that of classical equilibrium calorimetry. However, valuable conclusions can be drawn from data accurate to only ±15%. The present author and others have demonstrated that precision and accuracy of at least ±5% are attainable with careful DSC[2,4].

The effects of ring substitution on ionization constants and reactivity of aromatic acids are well known[5]. However, little information is available on the effects of such substitution on molecular order in the solid and melt phases. By application of a few simple rules (see Bondi[6]) it is possible to draw relatively specific conclusions about order, the degree of solid and melt phase hydrogen bonding, and the kind of order present in groups pendant to the ring.

A series of half esters of *o*-phthalic acid was prepared for the purpose of determining the change in solid phase order as the remaining acid group becomes more hindered. This series was chosen since thermodynamic data are available for a few monobasic aromatic acids. The contrast between monobasic acid data should give the maximum amount of information about solid and liquid phase structure.

EXPERIMENTAL

Preparation of the esters

The preparation of the half esters of *o*-phthalic acid is straightforward and the products are easy to obtain in high purity. An equimolar mixture of 99.99% *o*-phthalic acid and the appropriate alcohol was refluxed with 4% *p*-toluene sulfonic acid in spectral grade acetone for one hour. The product mixture was cooled to room temperature, mixed with water (50%) and neutralized with sodium hydroxide. The neutral aqueous solution was extracted three times with ligroin. The ligroin phase was evaporated and the product taken up in hot ethanol and filtered. The filtered ethanol solution was cooled slowly to produce long needle crystals. These were separated by filtration and recrystallized twice more. The identity of the product as the monoester was verified by a glass electrode titration in water. The analyses on the four esters indicated that the purity was better than 99.99%. This preparation was probably aided by the difficulty involved in making the diester. The overall yield after crystallization was ~55% in all cases. The actual yield of crude product was higher but not determined.

Differential scanning calorimetry

The samples after careful drying in a vacuum desiccator were weighed into Perkin–Elmer flat planchettes using a Cahn microbalance. The sample size was 2–3 mg. The calorimetric DSC runs were made at a heating rate of 10°C/min and a sensitivity of 4 mcal/inch with a Perkin–Elmer DSC-1B. The DSC-1B was calibrated with the heats of fusion of stearic acid (99.99 mole %) and freezing point grade benzene[1]. The transition temperatures were determined with a DuPont Differential Thermal Analyser (DTA) equipped with a capillary melting point cell. The DuPont apparatus was calibrated on the temperature axis by melting benzene, stearic acid, 99.98 mole % octadecane, and 99.98 mole % dotriacontane. This covered the working range of these experiments completely. The techniques of DSC and DTA were combined to take maximum advantage of the calorie and temperature measuring abilities of the two methods.

RESULTS

The methyl, butyl and 2-octyl esters melted in a single step to form the isotropic liquid. The isopropyl ester consisted of two solid phases which melted at 74.6 and 79.8°C, respectively. These temperatures are taken from the endothermal minima of the DTA trace. For the purposes of the ΔH and ΔS calculations, the merging areas were added together and the higher endothermal minimum temperature was taken as characteristic of the whole transition. The DSC and DTA results on the four esters measured are listed in Table I.

TABLE I

THERMODYNAMIC PROPERTIES OF SOME HALF ESTERS OF *o*-PHTHALIC ACID

Compound	*DTA transition temperatures (°C)*[a]			*ΔH (kcal/mole)*	*ΔS (cal/mole per °C)*	*Graphical code*
	T_b	T_m	T_e			
Methyl hydrogen *o*-phthalate	75.6	84.7	86.8	5.14	14.4	6
Isopropyl hydrogen *o*-phthalate	70.7	74.6 79.8	83.2	5.89	16.8	7
n-Butyl hydrogen *o*-phthalate	67.2	70.4	75.9	6.20	18.1	8
2-Octyl hydrogen *o*-phthalate	52.8	58.5	61.2	9.25	27.9	9

[a] T_b = temperature at onset of endotherm; T_m = temperature at minimum of endotherm; T_e = temperature at end of endotherm.

DISCUSSION

The temperatures of melting of the half esters decrease with increasing chain length. Points 6 to 9 of Fig. 1 represent the esters and fall on a reasonably smooth curve. This indicates that the order in the solid phase is decreasing with increasing chain length or molecular weight of the ester[6]. By analogy, benzoic acid (point 1) and toluic acid (point 2) should be related to the half esters. Benzoic acid should exhibit the highest melting point due to hydrogen bonding in the solid phase. Toluic acid should exhibit a melting point intermediate between benzoic and methyl hydrogen phthalate. This is, indeed, the case (see Fig. 1 and Table II). Cinnamic acid (point 3 of Fig. 1), due to the lessened electronic effect of the benzene ring and steric factors, should have a more hydrogen bound solid. This also agrees well with the findings in

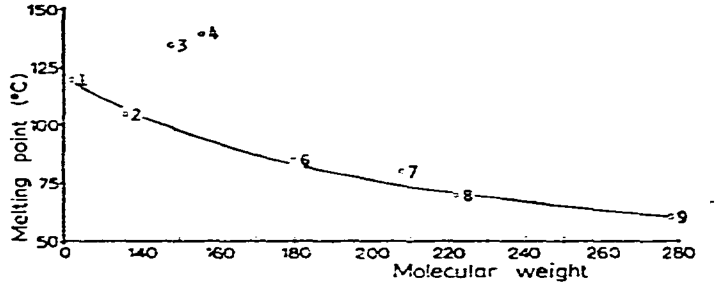

Fig. 1. Effect of substitution on fusion temperature of some substituted aromatic acids. For graphical code see Tables I and II.

Fig. 1. The *o*-chlorobenzoic acid (point 4 of Fig. 1) has about the same steric hindrance as *o*-toluic acid and methyl hydrogen phthalate. However, the electronic effect of the *o*-chlorine will alter the ionization of the carboxylic acid group in favor of a more ordered solid phase. A true aromatic ester such as methyl cinnamate, Table II, should show no relationship to the acid series when compared on the basis of melting point. This is the case.

TABLE II

THERMODYNAMIC CONSTANTS OF SOME AROMATIC ACIDS[a]

Compound	T_m (°C)	ΔH (*kcal/mole*)	ΔS (*cal/mole per °C*)	*Graphical code*
Benzoic acid	121.8	4.14	10.5	1
o-Toluic acid	103.7	4.82	12.8	2
Cinnamic acid	133.0	5.41	13.3	3
o-Chlorobenzoic acid	140.2	6.15	14.9	4
Methyl cinnamate	34.5	4.67	15.2	5

[a] Calculated from values given in Ref. 1.

Several factors can affect the magnitude of the total entropy of fusion[6]. In general, association in the liquid phase, restriction of rotation in the liquid phase, and disorder in the solid phase will *reduce* the total entropy of fusion. Hydrogen bonding in the solid phase, ionic interaction in the solid phase, restricted rotation in the solid phase and increased rotational possibilities in the liquid phase will *increase* the total entropy of fusion. Serious difficulties arise with these simple statements when compounds of greatly differing crystal configuration or functionality are compared. However, when the functionality is roughly the same, these rules can be powerful tools in the study of solid and liquid order of a related series.

The transition entropies of the four half esters (points 6 to 9) fall on a smooth curve (see Fig. 2). The curve appears to increase in slope above the n-butyl ester (point 8) as progressively more of the solid phase order is centered around the aliphatic ester chain, *i.e.*, the esters become more aliphatic and less aromatic with increasing molecular weight in the solid phase.

The entropy/molecular weight curve of the n-alkanes is very steep. That is, each additional CH_2 group greatly affects the total order of the solid phase. Additional substitution about the benzene ring affects the geometry of the solid order very little, if any[6], until a globular configuration is attained. Entropy change is minimized between solid and liquid in nearly spherical molecules[7].

The hydrogen bonding around the polar carbonyl group of benzoic acid causes association in the melt. This results in a low entropy of transition. This is partially compensated by some association as well as in the solid phase. The presence of the monoester group in the half esters brings a paraffinic order to the solid phase. The transition entropies compared to *o*-toluic acid, cinnamic acid, *o*-chlorobenzoic acid

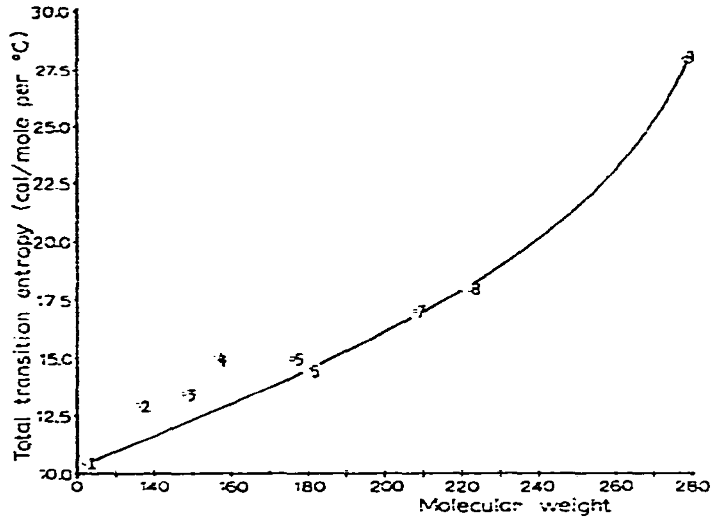

Fig. 2. Effect of substitution on the entropy of fusion of some substituted aromatic acids. For graphical code see Tables I and II.

and even methyl cinnamate are low (see Fig. 2). After the ester chain has attained a length of eight carbons or more, the melting properties and entropy of fusion become distinctly paraffinic.

CONCLUSIONS

The temperatures and entropies of fusion of the half esters of *o*-phthalic acid show a clear interrelationship with increasing chain length. The series, when compared to other aromatic acids, shows a clear shift away from acid hydrogen bonding in both the solid and melt phases. The effect of the ester side chain on the electronic distribution in the benzene ring and remaining acid group is clearly illustrated when the series is compared to *o*-chlorobenzoic acid and *o*-toluic acid. The series represents a continuous modification of the aromatic properties of the crystal lattice up to the 2-octanoate ester. Above this chain length, the solid and melt phase are distinctly aliphatic in nature.

REFERENCES

1 C. D. Hodgman, R. C. Weast, R. S. Shankland and S. M. Selby (Eds.), *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, 44th edn., 1963, p. 2409.
2 E. S. Watson, M. J. O'Neill, J. Justin and N. Brenner, *Anal. Chem.*, 36 (1964) 1233.
3 P. E. Slade and L. T. Jenkins (Eds.), *Techniques and Methods of Polymer Evaluation*, Vol. 2, Dekker, New York, 1970, p. 1.
4 E. M. Barrall II and R. D. Diller, *Thermochim. Acta*, 1 (1970) 509.
5 Jack Hine, *Physical Organic Chemistry*, Mc Graw-Hill, New York, 2nd edn., 1962, p. 81.
6 A. Bondi, *Chem. Rev.*, 67 (1967) 565.
7 Wen-kuei Wong and E. F. Westrum, Jr., *J. Phys. Chem.*, 74 (1970) 1303.