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Note

DSC STUDIES OF NAPHTHALENE STYPHNATES

F. SHAHIDI

Department of Chemistry, University of Toronto, Toronto, Ont. M5S 1A1 (Canada)

P.G. FARRELL

Department of Chemistry, McGill University, Montreal, Que. H3A 2K6 (Canada)

F. CASELLATO, C. VECCHI and A. GIRELLI

Stazione Sperimentale per i Compustibili, 20097 San Donato Milanese, Milan (Italy)

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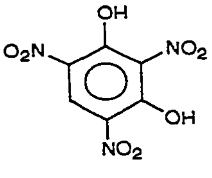
Thermal stabilities of addition compounds between aromatic hydrocarbons or their derivatives and nitroaromatic or anhydride acceptors by means of differential scanning calorimetry have received considerable attention in recent years [1—4], and the factors which determine the thermal stability of such crystalline charge-transfer complexes have been quantitatively known for sometime [5]. Among the nitroaromatic acceptors, trinitrobenzene (TNB), s-trinitrophenol (picric acid, PA) and trinitroresorcinol (styphnic acid, I) have been used extensively to form molecular complexes for the purposes of identification, separation and purification of aromatic hydrocarbons or their derivatives [6,7]. The results obtained to date, generally favor the idea that the contribution of the charge-transfer interactions (electronic factors) to the enthalpies of fusion are minor. Reticular forces governed by molecular factors of the donor and acceptor as well as crystal lattice forces play a major role in establishing the thermal behavior of the complex. This conclusion is also reached from our recent electrochemical studies of standard state thermodynamics of a number of arene picrates [8,9] and naphthalene styphnates [10]. To verify possible correlations of thermal behaviour as determined by differential scanning calorimetry and the standard state thermodynamic parameters, we have measured the enthalpies of fusion for a series of mono-substituted naphthalene styphnates and report our results here.



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EXPERIMENTAL

Materials and complexes

All the compounds used (donors or styphnic acid) were commercial products with the exception of hydroxymethylnaphthalenes which were obtained by lithium aluminium hydride reduction of the corresponding carboxylic acids. They were all recrystallized or redistilled prior to use in order to have melting or boiling points in agreement with the literature.

Styphnates were formed by mixing hot acetic acid solutions of equimolar amounts of styphnic acid and the donors and allowing the resulting mixture to cool slowly, whereupon the complexes were crystallized. The melting points obtained in DSC studies were all at or above the reported melting points [11].

DSC studies

Calorimetric measurements were performed using an indium (99.999% purity) calibrated Perkin-Elmer instrument, Model 1B. Between 2 and 6 mg of sample were sealed in aluminium pans and heated from room temperature to complete melting of the sample. A heating rate of 16°C min^{-1} and instrument sensitivity of 8 mcal sec^{-1} were used. The melted samples were cooled and kept at room temperature for about 1 h to allow complete recrystallization and then reheated in the calorimeter. At least three heating—cooling cycles were used.

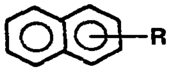
RESULTS AND DISCUSSION

The melting points, T_m, enthalpies, ΔH_f, and entropies, ΔS_f, of fusion of the mono-substituted naphthalene styphnates are assembled in Table 1. From the data presented, it is apparent that melting temperatures, ΔH_f and ΔS_f values for the 2-substituted compounds are higher than those for their 1-substituted analogues. The ΔH_f differences between the styphnates of 1- and 2-substituted naphthalenes primarily arise from the difference between the contribution of the heats of fusion for the donors. The 2-substituted naphthalenes are solid and hence contribute significantly to the ΔH_f for their corresponding styphnates, whereas the 1-substituted donors are generally liquid and do not have any significant contribution to the ΔH_f of their complexes.

While the melting points of the complexes generally lie between that of styphnic acid and those of the corresponding donors, the ΔH_f for the styphnates are generally larger than either the acceptor or the donor molecules as observed for other series of addition compounds [2,4]. It is also of interest to note that ΔH_f for naphthalene styphnate is larger than that for naphthalene picrate. This may be due to the fact that ΔH_f for styphnic acid is nearly twice as large as ΔH_f for picric acid [1] and the contribution of the enthalpy of fusion of the acceptor to that of the complex may explain the observed difference.

TABLE 1

Temperatures, enthalpies and entropies of fusion of molecular complexes of naphthalenes,



with styphnic acid

R	T_m (C)	ΔH_f (kJ mole^{-1})	ΔS_f (J mole^{-1} K^{-1})
H	165.4 ± 0.4	47.3 ± 0.4	108
1-CH_3	128.0 ± 1.0	34.7 ± 0.8	86.5
2-CH_3	128.6 ± 0 5	41.4 ± 0.4	103
1-OCH_3	126.7 ± 0.5	41.0 ± 0.6	101
2-OCH_3	142 7 ± 0.5	51.5 ± 0.7	125.5
1-F	119.9 ± 0.7	23.8 ± 2.3	61
2-F	118.7 ± 0.6	30.5 ± 0.6	78
1-Cl	123.0 ± 1.0	38.7 ± 1.0	98
2-Cl	134.3 ± 0.4	50.6 ± 0.4	125.5
1-Br	113.0 ± 1.0	37.8 ± 0.4	98
2-Br	122.4 ± 0.4	44.6 ± 0.4	113
1-I	91.5 ± 0.5	17.4 ± 1.0	50.5
2-I	114.7 ± 0.3	24.7 ± 0.2	64
1-CN	73.5 ± 0.7	34.7 ± 0.4	100
2-CN	121.9 ± 0.5	43.1 ± 0.6	109
1-CH_2OH	142.5 ± 0.6	46.4 ± 0.3	111
2-CH_2OH	172.9 ± 0.4	49.8 ± 0.5	112
1-$CO_2C_2H_5$	80.3 ± 0.5	30.1 ± 1.2	85
1-CHO	85.0 ± 0.5	30.1 ± 1.2	84
2-OH	172.9 ± 0.4	49.8 ± 0.5	112

As noted for other series of organic molecular complexes [2,12], no relationships are apparent between the thermodynamic data and structural parameters of the donors and the present data. Extrapolation of the solid state data (ΔG^0) for styphnate formation obtained electrochemically [10], to their melting temperatures in general yields positive values for ΔG^0. This is not unexpected, since the main contribution to the observed thermal stability of a complex is due to the crystal lattice and steric interactions, and the coupling energy or charge-transfer forces have only minor contribution to the total energy [13]. Similar conclusions may be reached from a comparison of the values of ΔS_f obtained here and the standard state entropies of formation, ΔS^0, for the same styphnates, where a general trend to increased $-\Delta S^0$ values with increasing ΔS_f is observed, especially for the 1-substituted donors. Further support for the low contribution of complexing interactions to the observed enthalpies of fusion is obtained from values of enthalpies of formation, ΔH^0, in the solid state (ca. 3—9 kJ mole^{-1}) and from the data shown in Table 1. The ΔH^0 values are considerably less than the measured values for ΔH_f.

The data presented here therefore imply that charge-transfer forces play only a minor role in determining the stabilities of the styphnates in the solid state.

ACKNOWLEDGEMENTS

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