Isotope Effects in Molecular Complexes of Naphthalene

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Summary Measurements of the free energy of complex formation between naphthalene or perdeuterionaphthalene and either picric acid or styphnic acid (2,4,6-trinitroresorcinol) show significant isotope effects, the deuteriated donor forming the stronger complex in each case at all temperatures studied.

The structures and properties of organic donor–acceptor, or charge-transfer, complexes in the solid state are of considerable interest in the continuing search for 'organometals' or organic semiconductors.[1] Whereas considerable structural information is now available from crystallographic studies on a wide variety of such complexes,[2,3] relatively little thermodynamic data pertaining to the stability of these molecular compounds exist.[4,5] In the course of our studies of the thermodynamics of charge-transfer complex formation between aromatic hydrocarbons and nitro-aromatic acceptors we have observed equilibrium, secondary isotope effects for complexes of naphthalene and its perdeuterio-derivative with picric and styphnic acids, and present here a preliminary report of these data.

Studies of the free energies of formation of naphthalene and $[^2H]_8$naphthalene picrates were made by the electrochemical method first described by Brönsted,[6] using aqueous ethanol as the solvent, and analogous measurements were made for the corresponding styphnates.† Entropy values were obtained from the temperature variation of the e.m.f. difference using a least-squares method and thence enthalpy data by means of the Gibbs-Helmholtz equation. The measured e.m.f. values are displayed in the Figure, and derived thermodynamic

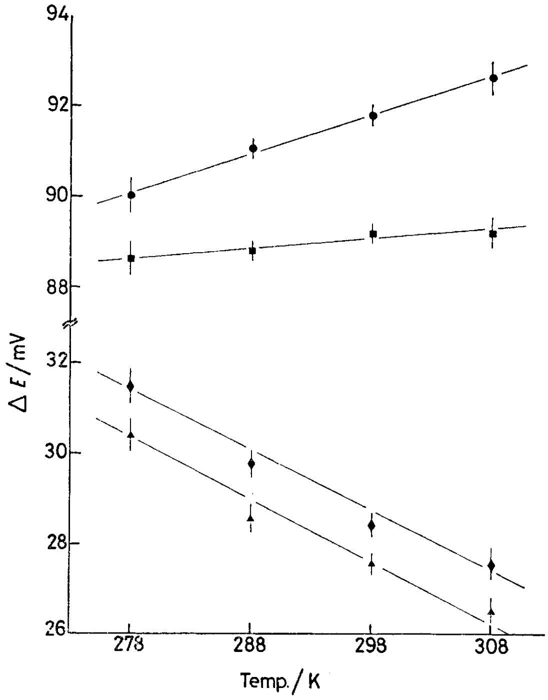

Figure. Temperature variation of the e.m.f. differences for complex formation: ■, naphthalene picrate; ●, $[^2H_8]$naphthalene picrate; ▲, naphthalene styphnate; ◆, $[^2H_8]$naphthalene styphnate.

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† Full details of the experimental technique for picrates have been previously described (ref. 5).

parameters at 298 K are given in the Table. Complex stoicheiometries were 1 : 1 in each case.

Table. Thermodynamic parameters for complex formation at 298 K

Compound	$-\Delta G^{\ominus}_{298}$/ kJ mol^{-1}	$-\Delta S^{\ominus}$/ J mol^{-1} K^{-1}	$-\Delta H^{\ominus}_{298}$/ kJ mol^{-1}
Picrates			
$C_{10}H_8$	8·60 ± 0·02	−1·9 ± 0·4	8·05 ± 0·15
$C_{10}D_8$	8·85 ± 0·02	−8·1 ± 0·5	6·45 ± 0·15
Styphnates			
$C_{10}H_8$	2·66 ± 0·02	11·5 ± 1·4	6·10 ± 0·45
$C_{10}D_8$	2·74 ± 0·02	13·0 ± 1·1	6·60 ± 0·35

From the picrate results presented in the Figure it is evident that the [$^{2}H_{8}$]naphthalene complex has the greater free energy of formation at any of the temperatures studied, and also that the resulting positive entropy of formation is greater for this complex. The values for the naphthalene complex compare fairly well with literature data.[6] Values for the styphnates also indicate a stronger interaction between the acceptor and [$^{2}H_{8}$]naphthalene but the derived entropies are negative for these complexes. As expected from steric considerations[7] and the electron releasing character of the OH group, styphnic acid forms weaker complexes than does picric acid.

The observed hydrogen isotope effects, $\Delta G^{\ominus}_{298,D}/\Delta G^{\ominus}_{298,H}$, are thus greater than unity, as expected, and are in accord with both the greater electropositivity of deuterium and the lesser amplitude of C–D vibrations.[8] They may be contrasted with earlier reported 'apparent' isotope effects in charge-transfer complexes, which gave $K_D/K_H < 1$ and were ascribed to the failure of Beer's law in the systems studied[9] (chloranil–toluene,[10] chloranil–*m*-xylene,[10] tetracyanoethylene–benzene[9]). The reported ionization potentials of naphthalene and [$^{2}H_{8}$]naphthalene are almost identical and it is thus improbable that the results arise from this cause.[11]

The positive entropies of complex formation for the picrates studied here are in accord with our findings for a variety of aromatic hydrocarbons,[12] and presumably arise in part because of the stacking of donor and acceptor in alternate layers, together with a contribution from any disorder in the crystals.[2] Although McCrone has reported polymorphism in styphnic acid itself,[13] there is no detailed structural information for this compound or any of its complexes[14] to permit meaningful interpretation of the entropy or enthalpy data obtained for the styphnates.

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