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Temperature dependence of the electron spin concentration in complexes of iodine with aromatic hydrocarbons

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The pyrene-iodine and perylene-iodine compounds have often been cited as primary and relatively rare examples of charge transfer complexes for which a good correlation is found between the temperature dependence of the electron spin concentration and the d.c. electrical conductivity[1-6]. It has not been established whether this behavior is inherently related to the thermodynamic stability and composition of these complexes and whether polymorphic forms exist which exhibit significantly different electronic behavior. Polymorphic forms of other complexes exhibiting varying properties have been observed[4, 5, 7-9].

Perylene-iodine and pyrene-iodine complexes may be prepared by (1) crystallization from solution as was done in the above studies[1-3]; (2) mixing the hydrocarbon with a stoichiometric quantity of iodine at 80°C (direct-mixing method); (3) absorption of iodine vapor by the hydrocarbon at 80°C (vapor-absorption method). It was of interest to observe the effect of the preparative method on the thermodynamic stability and ESR spectra of the complexes.

Complexes were prepared as indicated in Table 1. A coronene-iodine complex was prepared for comparison because of its anomalously low electrical conductivity[10]. The degree of crystallinity of the samples was assessed by examining their X-ray diffraction patterns. The results in Table 1 indicate that precipitation from solution produces the most crystalline complexes.

The enthalpies and free energies of formation of the two complexes prepared by crystallization from solution were determined by measuring the vapor pressures of iodine over

mixtures of complex and hydrocarbon at temperatures of 330-370°K. The results were compared to data previously obtained on $\text{Py}(\text{I}_2)_2$ and $\text{Pe}(\text{I}_2)_{1.5}$ prepared by direct mixing[11]. The vapor pressure data for the $\text{Py}(\text{I}_2)_2$ samples are compared in Fig. 1. For both the $\text{Py}(\text{I}_2)_2$ and $\text{Pe}(\text{I}_2)_{1.5}$ complexes, the enthalpies and free energies of formation were found to be independent of the method of preparation. It was previously observed that the enthalpies of formation of a number of hydrocarbon-iodine complexes including those of coronene, perylene and pyrene were in the range of -12 to -15 kcal mole I_2 [11].

The results of the ESR study of spin concentration are shown in Fig. 2. Since it was not experimentally possible to accurately determine the absolute spin concentrations, the data are plotted relative to the spin concentrations at 111°K (black circles in Fig. 2). Relative spin concentrations were determined using a dual cavity, a Mn standard sample and by assuming almost free spins after eqn (3) of Singer and Kommandeur[2]. Experimental line-shapes for each sample were found to be Lorentzian for at least five line widths. Saturation curves were run on each sample at the lowest temperatures used and the maximum allowable microwave power was determined. The susceptibility of each sample relative to that at 111°K was determined using eqn (4) of Singer and Kommandeur.

The $\text{Py}(\text{I}_2)_2$ and CnI_2 complexes formed by direct mixing and vapor absorption have spin concentrations which are independent of temperature, i.e. susceptibility is proportional to $1/T$ and are estimated to be within an order of magnitude of each other. The spin concentration of the $\text{Py}(\text{I}_2)_2$ crystallized from solution increases sharply at temperatures above 160°C in agreement with previous data[2]. The $\text{Pe}(\text{I}_2)_{1.5}$ and $\text{Pe}(\text{I}_2)_{2.9}$ complexes formed by

Table 1. Method of preparation of the hydrocarbon-iodine complexes

Compound	Preparation	X-ray powder diffraction pattern
Pyrene (Py)	Crystallization from alcohol	Strong peaks
Perylene (Pe)	Crystallization from benzene	Strong peaks
$\text{Py}(\text{I}_2)_2$	Crystallization from CCl_4	Moderate peaks
$\text{Py}(\text{I}_2)_2$	Direct mixing	No peaks
$\text{Py}(\text{I}_2)_2$	Vapor absorption	No peaks
$\text{Pe}(\text{I}_2)_{1.5}$	Crystallization from benzene	Weak peaks
$\text{Pe}(\text{I}_2)_{1.5}$	Direct mixing	No peaks
$\text{Pe}(\text{I}_2)_{2.9}$	Direct mixing	Weak peaks
$\text{Pe}(\text{I}_2)_{2.9}$	Vapor absorption	Weak peaks
CnI_2	Direct mixing	Weak peaks

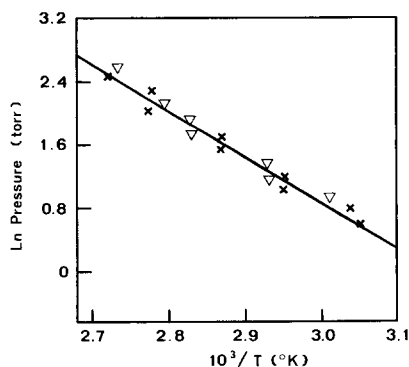


Fig. 1. Vapor pressures of pyrene-iodine complexes, $\text{Py}(\text{I}_2)_2$: \times , prepared by direct mixing; ∇ , prepared by crystallization from CCl_4 solution.

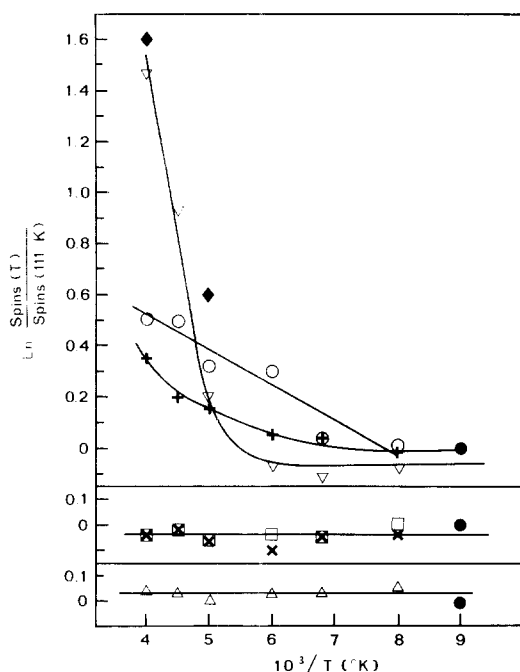


Fig. 2. Relative spin concentrations as a function of temperature: Δ , coronene-iodine complex, CnI_2 (direct mixing); \times , pyrene-iodine complex, $Py(I_2)_2$ (direct mixing); \square , pyrene-iodine complex, $Py(I_2)_2$ (vapor absorption); $+$, perylene-iodine complex, $Pe(I_2)_{2.9}$ (direct mixing); \circ , perylene-iodine complex, $Pe(I_2)_{1.5}$ (direct mixing); ∇ , pyrene-iodine complex, $Py(I_2)_2$ (crystallization from CCl_4); \blacklozenge , pyrene-iodine complex, $Py(I_2)_2$ (crystallization from CCl_4) data taken from Ref. [2].

direct mixing show slightly temperature dependent spin concentrations as was observed for $Pe(I_2)_{1.5}$ crystallized from benzene[2].

A general description of the nature of the iodine complexes of the aromatic hydrocarbons under discussion must take into account the following experimental observations. (1) The heat of formation of a complex is not dependent on its method of preparation; (2) The complexes of a number of different hydrocarbons have approximately the same value for the heat of formation; (3) The spin concentration of a complex may be strongly dependent on its method of preparation; (4) The electrical conductivities of the pyrene-iodine and perylene-iodine complexes are fairly high (10^{-1} – 10^{-3} (Ω cm) $^{-1}$) regardless of method of

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preparation; (5) The electrical conductivity of the coronene-iodine complex is very low (10^{-8} (Ω -cm) $^{-1}$) regardless of method of preparation; (6) The temperature dependence of the conductivity parallels that of the spin concentration for perylene-iodine and pyrene-iodine complexes crystallized from solution.

Consideration of these factors indicates the following picture. The complexes are basically "molecular" i.e. their stability depends primarily on local interactions between iodine molecules and adjacent hydrocarbon molecules. Local charge transfer which occurs between adjacent iodine and hydrocarbon molecules possibly as a result of lattice irregularities is incidental to the chemical bonding. The mechanism for electrical conductivity and spin concentration are not closely related unless the degree of long range regularity and periodicity of the lattice is sufficiently high to result in the formation of a band structure. This occurrence does not measurably influence the thermodynamic stability of the complexes since the enthalpy and free energy of formation are not affected.

The CnI_2 and the poorly crystalline $Py(I_2)_2$ complexes have similar spin concentrations but differ by orders of magnitude in conductivity. The activation energy for electron transport in CnI_2 may be high because of the relatively low concentration of iodine[12]. In the case of the $Pe(I_2)_{2.9}$ complex in Fig. 2 and the $Py(I_2)_2$ complex crystallized from solution, the temperature dependence of the spin concentration indicates that more than one mechanism is operative. Highly crystalline regions in which a conduction band is present may be interspersed with regions in which only localized charge separation occurs.

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Induced intense circular dichroism spectra

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Substantial interest has recently been generated in the area of chiral transition metal organometallic complexes[1]. The initial studies demonstrated that resolution of such complexes was possible and in many cases are fairly stable to racemization. Some

more recent work has used optically active metal complexes in mechanistic studies[2], much in the way that organic chemists have used optically active carbon compounds for years. For example, the photolytic decarbonylation of $(\eta^5-C_5H_5)Fe(CO)$