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Chemical Stability of Complexes of Iodine with 2,2-Diphenyl-1-picrylhydrazyl and Naphthalene

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Iodine vapor pressure data were obtained on the solid complex formed between 2,2-diphenyl-1-picrylhydrazyl and iodine and on liquid solutions of naphthalene and iodine. The solidus–liquidus curve for naphthalene–iodine was determined. Electrical conductivity measurements were made on 2,2-diphenyl-1-picrylhydrazyl-iodine liquid solutions. The results of this study are compared to data previously obtained on complexes of iodine with polynuclear aromatic hydrocarbons.

Introduction

Iodine forms complexes with a variety of organic compounds in solution and in the solid state (*1*, *2*). Electrical and magnetic measurements on the complexes in the solid state give evidence that a small but significant amount of electron transfer occurs between the organic molecules and the iodine molecules (*1*–*3*). From iodine vapor pressure measurements, we have determined the free energies and enthalpies of formation of complexes of iodine with six polynuclear aromatic hydrocarbons containing between four (pyrene) and ten (ovalene) condensed benzene rings (*4*, *5*). The enthalpies of complexation were found to be in the range of -10 to -15 kcal/mole I_2. The similar and relatively low values for the enthalpies of reaction coupled with the observation that these same complexes differ widely in their electrical and magnetic properties (*3*, *6*) indicates that charge transfer does not play a significant role in the chemical bonding, which is probably of the vander Waals type.

Kawabe *et al.* (*7*) have studied the electrical and magnetic properties of the complex formed between iodine and the stable free radical 2,2-diphenyl-1-picrylhydrazyl ($(C_6H_5)_2N\dot{N}C_6H_2(NO_2)_3$). They indicate that iodine can be added to 2,2-diphenyl-1-picrylhydrazyl (DPPH) in a continuous manner up to a limiting composition of two iodine molecules per DPPH molecule. A continuous decrease in magnetic susceptibility is observed as the iodine is added which they interpret as resulting from the transfer of unpaired electrons from DPPH to iodine. Approximately one electron per DPPH molecule is transferred at an I_2/DPPH molecular ratio of 2.

A primary objective of the present investigation was to determine if electron transfer plays an important role in the chemical bonding between DPPH and iodine molecules. It was also of interest to determine if a continuous solid-solution region exists

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between an I_2/DPPH molecular ratio of 0 and 2. In the case of the complexes formed between iodine and polynuclear aromatic hydrocarbons, only compounds of definite composition were observed (*4, 8*).

An additional objective of the present investigation was to make some comparison of the properties of the complexes in the liquid state with those in the solid state. To this end, the liquidus–solidus curve for naphthalene–iodine was determined and iodine vapor pressure measurements were made on molten naphthalene–iodine compositions. Electrical conductivity measurements were performed on DPPH–I_2 molten compositions and are compared to conductivity data on molten naphthalene–iodine and pyrene–iodine compositions obtained previously (*9*).

Experimental

2,2-Diphenyl-1-picrylhydrazyl and naphthalene were obtained in the highest purity available (98%) from the Aldrich Chemical Co. of Milwaukee, Wisconsin. DPPH was recrystallized from chloroform and carbon tetrachloride. It was evacuated at 80°C for 48 hr to remove traces of the solvent present in the form of solvent–DPPH complex (*10*). The naphthalene was recrystallized from ethyl ether. Reagent-grade iodine was obtained from the Fisher Scientific Co. of Fairlawn, N.J., and was purified by sublimation.

The DPPH–iodine compositions were prepared by sealing a powdered mixture of DPPH and iodine in the desired mole ratio into an evacuated glass tube and heating at 60°C for 24 hr.

Iodine vapor pressure measurements on the DPPH–iodine compositions were first attempted using the manometric system employed successfully for the polynuclear aromatic hydrocarbon complexes (*5*). It was found, however, that constant vapor pressure values were not attainable. A slow increase in pressure with time was observed. It is possible that solvent molecules from the recrystallization were still present or that DPPH slowly decomposes with the formation of volatile products.

A colorimetric technique previously used for the hydrocarbons (*4*), sensitive to iodine vapor only, was employed. In the present investigation a Gilford Instrument Co. spectrophotometer was used. The spectrophotometer cell compartment could be heated to a temperature of 95°C by pumping heated ethylene glycol through special metal coil assemblies attached to both sides of the cell compartment. The temperature inside the cell compartment was monitored using a copper-constantan thermocouple. Absorption at a wavelength of 5200 Å was found to give the best results. Other details of the technique have been previously described (*4*).

The vapor pressures of iodine measured using this colorimetric technique were constant with time. It is, therefore, evident that the interaction of DPPH with iodine was not effected by whatever factors caused the slow increase in total vapor pressure observed using the manometric technique.

The solidus–liquidus curve for the naphthalene–iodine system was determined from temperature–time plots of the cooling of the molten solutions. Powdered naphthalene–iodine mixtures were placed in a small bulb at the end of a 6-in. long, 7-mm i.d. Pyrex tube. A concentric, 5-mm o.d., closed-end Pyrex tube containing a copper-constantan thermocouple in a pool of mercury was inserted into the mixture. Before insertion, the inner glass tube was wrapped with teflon tape to make a tight sliding seal with the outer glass tube. The naphthalene–iodine mixture in the tube assembly was heated in an oil bath until the mixture became molten. The tube assembly was removed from the bath. A plot of temperature versus time was recorded on a millivolt recorder attached to the thermocouple.

Phase changes were detected as abrupt changes in slope in the temperature–time plots. The freezing points of naphthalene and of iodine determined by this method were within one degree of the values reported in the literature.

Results and Discussion

Iodine vapor pressure measurements were made on DPPH–I_2 molar ratios of 4 : 1, 3 : 1, 2 : 1, and 1 : 1 at temperatures of 65 to 95°C. The data are shown in Fig. 1 as logarithmic plots of vapor pressure vs reciprocal temperature. Although the temperature range is limited and the data show some scatter, it is evident that all the compositions give essentially the same results. We may, therefore, conclude that all the compositions tested are mixtures of DPPH and a single DPPH–I_2 complex. This complex has been shown by Kawabe and coworkers to have a DPPH–I_2 molecular ratio of 1 : 2 (*7*).

The enthalpy and entropy of complexation were calculated by least-squares analysis of the data to be −11.4 kcal/mole I_2 and −23.2 cal/K-mole I_2, respectively. For the polynuclear aromatic hydrocarbons studied previously (*4*, *5*), the enthalpies of complexation ranged from −10.1 kcal/mole I_2 to −15.3 kcal/mole I_2. A comparison of the data obtained on DPPH with those obtained on the hydrocarbons, pyrene, and pentacene (*5*), is shown in Fig. 2. The DPPH data fall in the middle of the range of the data obtained on the hydrocarbons. Therefore, it is likely that the bonding between DPPH and iodine is of the same type as that between the hydrocarbons and iodine. Charge transfer does not appear to play a significant role in the hydrocarbon–iodine bonding. It is, therefore, probably not a significant factor in the DPPH–I_2 bonding. This is a surprising result considering that approximately one electron per DPPH molecule is transferred in the complex.

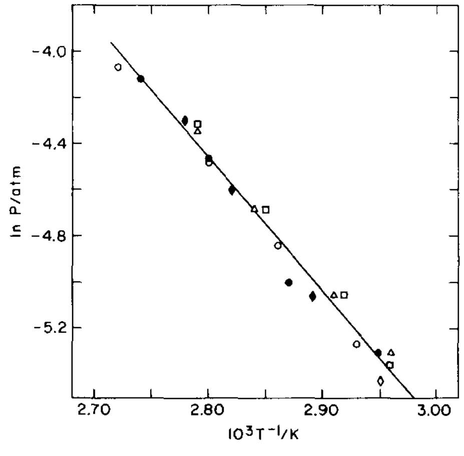

FIG. 1. Iodine vapor pressure data on different DPPH–I_2 molar ratios: □, 4 : 1; ◆, 3 : 1; ○, 2 : 1; ●, 2 : 1; △, 1 : 1.

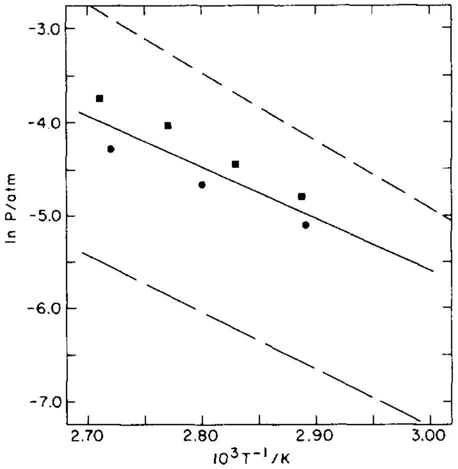

FIG. 2. Comparison of iodine vapor pressure data on complexes of iodine with DPPH, pentacene, pyrene, and naphthalene: continuous curve, DPPH; broken line, large segments, pentacene; broken line, small segments, pyrene; ●, 80 mole% naphthalene liquid solution; ■, 65 mole% naphthalene liquid solution.

These conclusions about the extent of charge transfer and its relationship to chemical bonding in the iodine complexes of DPPH and the hydrocarbons are tentative. More direct evidence concerning the extent of charge transfer obtained from single crystal X-ray diffraction and spectroscopic techniques would be very useful in quantitatively relating charge transfer to chemical bonding.

A question of interest concerning the iodine complexes is the nature of the bonding in the liquid state. The colorimetric technique could not be used to measure iodine vapor pressures over the hydrocarbon–iodine and DPPH–iodine complexes in the liquid state because melting occurs at too high a temperature for the experimental method to be applicable.

Naphthalene and iodine do not form a complex in the solid state. This is probably not due to a major difference between the chemical nature of naphthalene and the other polynuclear aromatic hydrocarbons. The free energies of complexation of the solid hydrocarbons with solid iodine range from near zero, in the case of pyrene, to a few kilocalories (negative) (5). It is likely that the free energy of complexation of solid naphthalene with solid iodine is slightly positive, i.e., a few kilocalories less negative than in the case of the other hydrocarbons.

It was observed experimentally that mixtures of iodine and naphthalene form liquid solutions at temperatures well below 100°C. The colorimetric method could, therefore, be used to measure iodine vapor pressures over iodine–naphthalene liquid solutions. It was first necessary, however, to establish the solidus–liquidus curve in the naphthalene–iodine system.

The results of the temperature–time study of the cooling of liquid solutions of naphthalene and iodine are shown in Fig. 3. The points on the liquidus–solidus curve were obtained from the first abrupt change in slope at each composition. A second abrupt change in slope was observed at the eutectic temperature, 64 ± 2°C. Below the liquidus–solidus curve only a mixture of solid naphthalene and solid iodine is present.

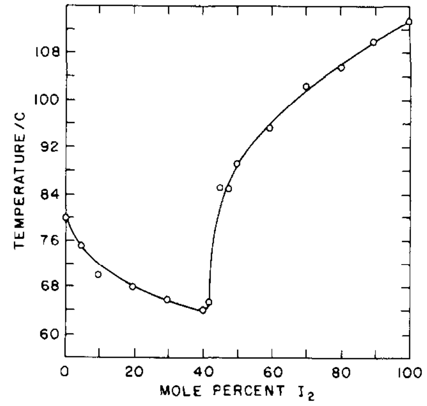

FIG. 3. Solidus–liquidus curve in the naphthalene–iodine system.

Two compositions, 20 and 35 mole% iodine, were selected for iodine vapor pressure measurements in the liquid region. A slight change in experimental technique from that used with DPPH–I_2 was required. In the latter case, a mixture of DPPH and the DPPH complex was placed on the bottom of the spectrophotometer absorption cell. When a mixture of naphthalene and iodine was placed on the bottom of the cell, creeping up the sides of the cell occurred when the mixture melted, interfering with the light path. Therefore, it was necessary to suspend a glass pan holding the mixture from the top of the cell using a piece of teflon tape.

Iodine vapor pressure measurements could only be made over a temperature range of about 20°C. The data obtained are shown in Fig. 2. The vapor pressures are very similar to those observed for the solid DPPH–I_2 mixtures. Partial molar enthalpies of solution of iodine calculated from the slopes of the $\ln P$ versus $1/T$ plots are -10 kcal/mole I_2 and -12 kcal/mole I_2 for the 35 and 20 mole% solutions, respectively

The similarity of the vapor pressure data on the naphthalene–iodine liquid solutions to those obtained on solid DPPH–I_2 and polynuclear aromatic hydrocarbon–I_2 complexes indicates that the chemical bonding between the organic molecules and iodine

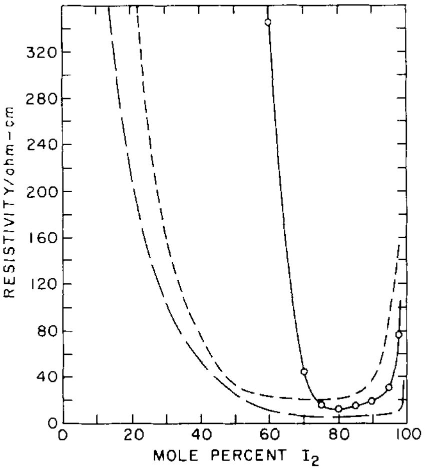

FIG. 4. Comparison of electrical resistivities of liquid solutions of iodine with DPPH, pyrene and naphthalene: ○, DPPH at 145°C; broken line, large segments, pyrene at 155°C; broken line, small segments, naphthalene at 120°C.

is similar in the liquid and solid states, with van der Waals forces probably playing the major role.

Electrical conductivity measurements on pyrene–iodine and naphthalene–iodine liquid solutions show that these solutions are fairly good electrical conductors over wide composition ranges (*9*). It was of interest to measure the electrical conductivity of DPPH–I_2 liquid solutions to observe the effect of the large degree of electron transfer. Conductivity measurements were made at 145°C. At this temperature, all DPPH–I_2 compositions are liquid. The experimental technique used was previously described (*9*).

The conductivity data on DPPH–I_2 are compared to those previously obtained on pyrene–iodine and naphthalene–iodine in Fig. 4. It is observed that the minimum resistivity is in the same range as that for pyrene–I_2 and naphthalene–I_2 (~10 ohm-cm). The composition range over which low resistivities are observed is narrower for DPPH–I_2. One does not observe enhanced conductivity in DPPH–I_2 as a result of extensive electron transfer. Thus, in its electrical behavior in the liquid state as well as in its chemical bonding, DPPH interacts with iodine in the same way as polynuclear aromatic hydrocarbons.

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