BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 3345—3346 (1976)

Phase Diagram of the Pyrene-Picryl Chloride System

Masaki BANDO and Yoshio MATSUNAGA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 19, 1976)

Synopsis. A differential scanning calorimetric study of the pyrene–picryl chloride system has revealed five molecular compounds with mole ratios of 1: 1, 4: 3, 2: 1, 3: 1, and 4: 1 respectively.

Most molecular compounds are equimolar in composition. Therefore, the phase diagrams of organic binary systems are generally simple. The pyrene-pyromellitic dianhydride system which forms three molecular compounds with ratios of 3: 1 or 2: 1, 1: 1, and 1: 3 respectively is known to be rather exceptional.[1] Such simplicity may be characteristic of organic systems but may be, at least in part, connected with the thaw-point-melting-point method employed in the determination of phase diagrams.[2] While solid–liquid equilibria give valuable information regarding the state of a system within the temperature limits of the diagram, the information obtained does not necessarily remain valid at lower temperatures. When solid-solid transitions, if any, are included in the examinations, the phase relations might be more complicated than previously reported. Studies of the anthracene–carbazole and naphthalene–2-naphthol systems made by Robinson and Scott seem to support such a postulate; however, neither of the systems gives a molecular compound.[3,4] The pyrene–picryl chloride system, which has been reported to form only an equimolar compound,[5] has been studied as our first choice along this line because of the following reasons. First, a solid-solid transition is known to occur in the molecular compound near 80 °C.[6] Secondly, the closely-related pyrene-picryl bromide system has been found to form two compounds with ratios of 1: 1 and 3: 2 respectively.[7]

Samples were prepared by melting mixtures with known ratios of the parent compounds. The composition is quoted in the mole percentage of the hydrocarbon. The melting points and transition temperatures were determined using a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C. X-Ray measurements on powdered samples were made at room temperature with a Toshiba recording diffractometer, Model ADG-301, using filtered copper radiation.

As is shown in Fig. 1, the phase relations in the region from 0 to 50 mol % are simple. A eutectic occurs at 12 mol % and 75 °C; these values are to be compared with 8 mol % and 73.5 °C reported by Shinomiya.[5] All the samples in the region from this point to 50 mol % show an endothermic peak due to the appearance of the liquid phase and also one at 81 °C due to a solid-solid transition in the equimolar molecular compound. Four more distinct compounds are formed in the region from 50 to 80 mol %. If the 1: 1 molecular compound melting at 154 °C were the only compound formed in this system, the endothermic peak due to the transition should be observed in the entire region from 50 to 100 mol %. As a matter of fact, the peak is observable only up to 57 mol %. Between 58 and 75 mol %, a new endothermic peak appears at 82—83 °C. Above 67 mol % an additional peak is found at 77 °C. This disappears by 80 mol %. These observations lead to the conclusion that the peak at 82—83 °C is due to a solid-solid transition in the 2: 1 compound (66.7 mol %) and that at 77 °C is due to a solid-solid transition in the 3: 1 compound (75 mol %). Two more phase boundaries are located at 57—58 mol % and at 80 mol % respectively, on the basis of the discontinuity of the transitions. These compositions correspond to molecular compounds with ratios of 4: 3 and 4: 1. Neither of them show solid-solid transitions near 80 °C.

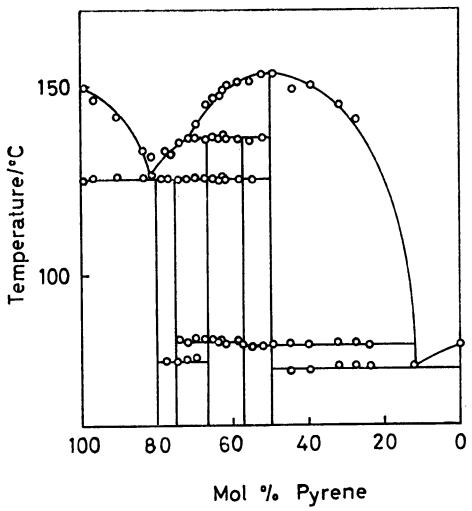

Fig. 1. The pyrene–picryl chloride phase diagram.

Turning to the solid-liquid equilibria in the region from 50 to 100 mol %, we see that only the equimolar molecular compound melts congruently. All the other four cease to be stable before their congruent melting points are reached. In the equilibrium diagram a eutectic point is cleary observed at about 81 mol % and 126 °C, and a peritectic point at about 71 mol % and 136 °C. It is evident that a eutectic conglomerate of pyrene and the 4: 1 molecular compound coexist in contact with the liquid at the former point. Shinomiya has assumed the eutectic point to be at 77 mol % and 125 °C.[5] Because of the formation of the 4: 1 compound this point cannot be at such a low percentage of the hydrocarbon. By visual examination, the thaw point in the region from 58 to 66 mol % was located not at 126 °C but at 136 °C; therefore, the molecular compound which undergoes decomposition into another compound and the liquid at the latter point was identified as the 2: 1 compound. The incongruent melting

* To whom inquiries may be addressed.

points of the 4: 1 and 3: 1 compounds are supposed to be slightly higher than the eutectic, but they are practically not distinguishable from each other. The endothermic peak observed at about 126 °C in the region from 50 to 66 mol % is nearly at the eutectic temperature. However, this must be attributed to a solid-solid transition in the 4: 3 compound, since the peak is not accompanied with liquefaction. This molecular compound also melts incongruently. Its peritectic point is located presumably very close to that of the 2: 1 compound. This conclusion is in accordance with Shinomiya's finding that the formation of liquid occurred at 135 °C in his 57.4 mol % sample.[5] If this observation was seriously taken into consideration, he could easily find the peritectic point in this system. Nevertheless, it should be emphasized that only two molecular compounds among the five may be found using the thaw-point-melting-point method.

The differences in the X-ray diffraction patterns between the equimolar molecular compound and the other four are appreciable. The crystal data of the 1: 1 compound have been determined by Herbstein and Kaftory.[8] The peak with a spacing of $a \sin\beta = 17.13$ Å is seen only in this compound. On the other hand, a spacing of about 10.6 Å, which is absent in the 1: 1 compound, is the longest in all the other compounds. The patterns of the compounds with stoichiometries other than 1: 1 are not very different from each other; however, the observed minor but definite difference is consistent with the existence of distinct compounds. The crystal structure of the stable red prisms of 3 pyrene: 2 picryl bromide has been described in terms of equimolar mixed stacks with alternating pyrene and picryl bromide molecules and interstial pyrene molecules steeply inclined to the stack axis.[7] It is likely that the hydrocarbon in the new phases of the present system also fills two different structural roles.

The authors wish to express their thanks to Professor Toshio Yokokawa for letting them use the X-ray diffractometer.

References

1) F. H. Herbstein and J. A. Snyman, *Phil. Trans. Roy. Soc. London*, **A 264**, 635 (1969).
2) H. Rheinboldt, *J. Prakt. Chem.* (2), **111**, 242 (1925).
3) P. M. Robinson and H. G. Scott, *Mol. Cryst. Liq. Cryst.*, **5**, 387 (1969).
4) P. M. Robinson and H. G. Scott, *Mol. Cryst. Liq. Cryst.*, **18**, 143 (1972).
5) C. Shinomiya, *Bull. Chem. Soc. Jpn.*, **15**, 259 (1940).
6) N. Inoue and Y. Matsunaga, unpublished work.
7) F. H. Herbstein and M. Kaftory, *Acta Crystallogr.*, **B 31**, 45 (1975).
8) F. H. Herbstein and M. Kaftory, *Acta Crystallogr.*, **B 31**, 60 (1975).