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On the Enantiotropic Transitions in the Phenanthrene Picrate

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Phenanthrene has long been known to form an equimolecular addition compound with picric acid.¹⁾ The presence of an enantiotropic transition at 106°C in this compound was noted by Kofler in 1944.²⁾ We newly observed the presence of another transition in the phenanthrene picrate. Contrary to the one reported by Kofler, the change from the high-temperature form to the low-temperature one is very slow in the new transition located at 77°C. As ordinary phenanthrene is often contaminated with an appreciable amount of anthracene, the effect of the impurity on the transitions was also examined. As will be described later, a reason why Kofler missed one of the transitions can be proposed on the basis of this examination.

Phenanthrene, Eastman white label, was boiled with maleic anhydride in xylene to remove any anthracene.³⁾ The picrate crystallized from benzene was mixed with anthracene picrate separately prepared, in various ratios (0.97—10.0 mol%) and then fused together. After annealing at room temperature for three days or longer, the specimens were examined by means of a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3°C/min. The heats of transition were estimated by comparing the peak areas with that for the transition in hexamethyl-

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1) C. Graebe, *Ann. Chem.*, **167**, 137 (1873).
2) A. Kofler, *Z. Elektrochem.*, **50**, 200 (1944).
3) J. Feldman, P. Pantages, and M. Orchin, *J. Amer. Chem. Soc.*, **73**, 4341 (1951).

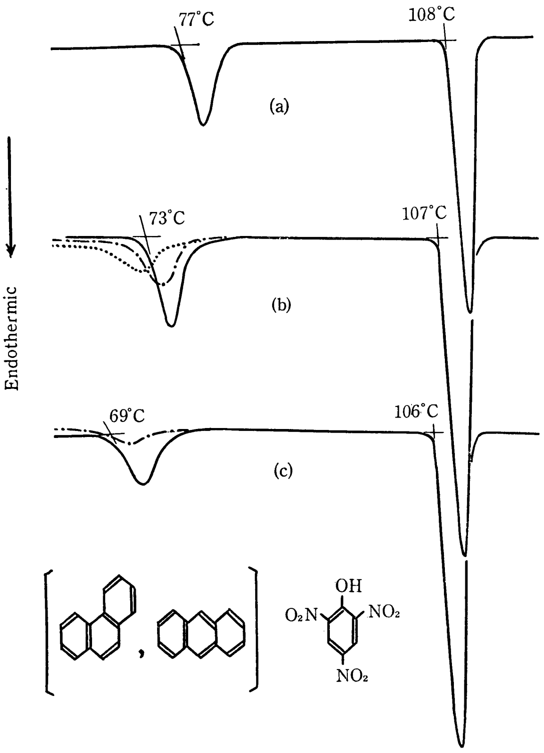

Fig. 1. The DSC thermograms of phenanthrene picrate annealed over one month (—), for one day (····), and for three days (-·-): (a) 18.8 mg of the pure specimen, (b) 22.3 mg of the specimen containing 0.97 mol% of anthracene picrate and (c) 22.8 mg of the specimen containing 3.12 mol% of anthracene picrate.

benzene, which is known to take place at 110.6°C with ΔH=0.422 kcal/mol.[4)]

The transitions in pure phenanthrene picrate are located at 77°C with ΔH=1.1 kcal/mol and at 108°C with ΔH=3.1 kcal/mol. The first transition cannot be observed in the second run if it is recorded immediately after the first heating. A similarly slow transition has been known to occur in anthracene picrate at about 85°C.[2)] As is shown in Fig. 1, both the first and second transition points move to lower temperature upon the addition of anthracene picrate. Although the heat of transition due to the second phase-change stays almost constant up to a 5 mol% addition of anthracene picrate, that due to the first phase-change decreases slightly to 0.8—0.9 kcal/mol in the range of 2—3 mol%. Furthermore, the higher the contamination with anthracene, the slower the rate of the recovery of the low-temperature form. After annealing for three days, which is long enough for pure phenanthrene picrate, the specimens containing 0.97—3.12 mol% anthracene picrate produce a peak area due to the first phase-change much smaller than that obtained after a prolonged annealing. In addition, it must be noted that the peak observed after a partial recovery appears at temperatures lower than that observed after the complete recovery. Above a 5 mol% addition of anthracene picrate, the first phase-change is no longer detectable even after over-one-month storage at room temperature. Thus, not only the magnitude of the heat of the newly-found transition, but also the rate of the recovery of the low-temperature form are very sensitive to contamination with anthracene. From these observations it would appear that the visual examination of this transition employed by Kofler is difficult if the phenanthrene contains anthracene in the order of one mol percent. On the other hand, the second phase-change in phenanthrene picrate remains even in the presence of 10 mol% anthracene picrate. Therefore, it seems likely that the discrepancy between the present observation and Kofler's can be ascribed to the difference in purity of the phenanthrene used.

[4)] M. E. Spaght, S. B. Thomas, and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).