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Effect of Polymorphic Transition on Molecular Diffusion in Some Molecular Complexes, as Evidenced by Exchange Reaction Rate and by Electrical Resistivity

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Synopsis. Marked increases in electron donor and acceptor-exchange reaction rates and also large differences in the temperature dependence of the electrical resistivity of polycrystalline compactions between the first and the second heating processes indicate the enhanced molecular diffusion near and above the polymorphic transition temperatures of some molecular complexes.

The appearance of isomorphous high-temperature forms upon polymorphic transitions in over twenty molecular complexes consisting of aromatic hydrocarbons and various electron acceptors has been ascribed to the onset of molecular rotation.[1] In this connection, these complexes bear some similarity to plastic crystals, which are composed of globularly shaped and orientationally disordered molecules. As plastic crystals are known to show diffusion coefficients approximately 10^4 times higher than normal crystals when compared at their melting points,[2] an appreciable increase of the translational mobility upon the transitions might be expected for the above-mentioned molecular complexes. Attempts were made to follow such changes in some selected complexes by measurements of electron donor and acceptor-exchange reaction rates covering the transition temperature and also by comparison of the electrical resistivity of polycrystalline compactions between the first and the second heating processes.

The following three 1 : 1 complexes seemed to suit the study of the exchange reactions because of their relatively low transition temperatures and large entropy changes: pyrene-2,4-dinitrotoluene (Py–DNT), 53.5 °C, 37 J mol^{-1} K^{-1}; pyrene-2,4,6-trinitrotoluene (Py–TNT), 59 °C, 36 J mol^{-1} K^{-1}; fluoranthene-2,4,6-trinitrochlorobenzene (Fl–TNC), 54 °C, 54 J mol^{-1} K^{-1}. The acceptors employed for the exchange reactions were 2,4,7-trinitrofluorenone (TNF) and 4,6-dinitrobenzofuroxan (DNBF). They are stronger as acceptors than any in the complexes and have melting points higher than those of the complexes. Because of the former condition, the complex formed by the exchange reaction gives a charge-transfer absorption band in a region separated from that of the original complex. The latter condition was expected to mean that the molecules in the added component compound would be less mobile than those in the complex. The donor-exchange reaction was examined with the combination of Fl–TNC and Py. Py is stronger as a donor than Fl and its melting

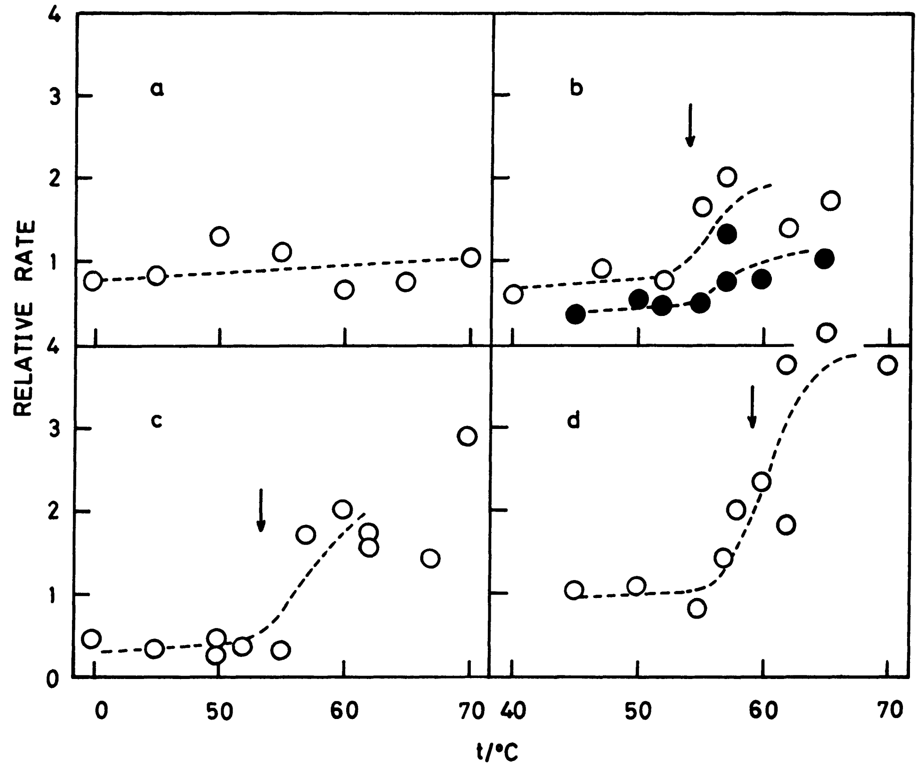

Fig. 1. Relative rates of the exchange reactions between (a) fluoranthene-3-nitrophthalic anhydride and 4,6-dinitrobenzofuroxan, (b) fluoranthene-2,4,6-trinitrochlorobenzene and 4,6-dinitrobenzofuroxan (○) or pyrene (●), (c) pyrene-2,4-dinitrotoluene and 2,4,7-trinitrofluorenone, and (d) pyrene-2,4,6-trinitrotoluene and 2,4,7-trinitrofluorenone.

point is higher than that of Fl–TNC.

The complex and the component compound to be added to the complex were separately ground, and then mixed in a weight ratio of 45 : 1 by grinding for short time. The mixed powdered sample, packed into a holder for reflectance measurements, was kept in a thermostat. The spectrum was recorded at intervals of 10 to 120 min by means of a Beckman DK 2A spectroreflectometer. The intensity (I) of the new charge-transfer band estimated by the Kubelka-Munk function was considered to be proportional to the concentration of the complex formed by the exchange reaction. The ratio was chosen to make the final reflectance not less than 20%. The plot of $\ln I/(I_\infty - I)$ against the reaction time gave a straight line at each temperature. The slope naturally depends on the absorption coefficient of the charge-transfer band; therefore, it may be taken as a measure of the reaction rate only for each complex.

In order to check the reliability of the procedure, the reaction between Fl-3-nitrophthalic anhydride and DNBF was studied. This complex exhibits no polymorphic transition in the measured temperature range and has a melting point lower than that of DNBF (136 °C *vs.* 172 °C). The rate appears to increase slightly by raising the temperature (see Fig. 1a). The results obtained with Fl–TNC complex are presented in Fig. 1b. Although the measured rates are rather scattered, one can clearly see an increase near and above the transition temperature indicated by the vertical arrow. Similar and more pronounced changes were observed with the reactions between the Py complexes and TNF shown in Figs. 1c and 1d.

The increase of reactivity during polymorphic transition has been noted by Hedvall.[3] He reported many examples demonstrating that the transition temperature or the temperature range coincides with the maximum reactivity. The explanation given by him is the appearance of unstable and highly-reactive transitional states during the transition. No such maximum rate could be found in the present cases; however, the observed rate increase is undoubtedly indicative of enhanced molecular diffusion upon the transition of the complex.

The electrical resistivity of polycrystalline compactions of the five complexes in this group examined earlier showed an abrupt decrease in the transition temperature range.[4] This observation resembles that made for some plastic crystals by Swiatkiewicz and Pigon.[5] Now, we wish to report that the behavior in the first heating process can be quite different from that described before if the compaction is made of a thoroughly powdered sample. The best example was provided with the Fl-2,4,6-trinitrophenol complex, which is transformed into the isomorphous form at 93.5 °C with an entropy of 42 J mol^{-1} K^{-1}. As is shown in Fig. 2, an encrease of the resistivity by a factor of about five was found in the first run just below the transition temperature. On the other hand, the change in the second heating process is normal and reproducible. The decrease in the transition temperature range is as much as by a factor of twenty. The marked difference between the two runs can be explained if one assumes that the conduction in the compaction, which is not yet heated to the transition temperature, predominantly arises from surface current. Then, the resistivity increase near the transition temperature may be attributed to the decrease of the surface area by rapid recrystallization due to the enhanced molecular diffusion. The electrical behavior observed in the second run reflects the bulk property of the complex. Similar but less drastic changes have been recorded with the following complexes: Fl–TNC, Fl–TNT, and Fl-4-nitrophthalic anhydride. The anomalous change near the transition temperature has been reported in the work of Swiatkiewicz and Pigon on plastic crystals, and has been ascribed also to the recrystallization.

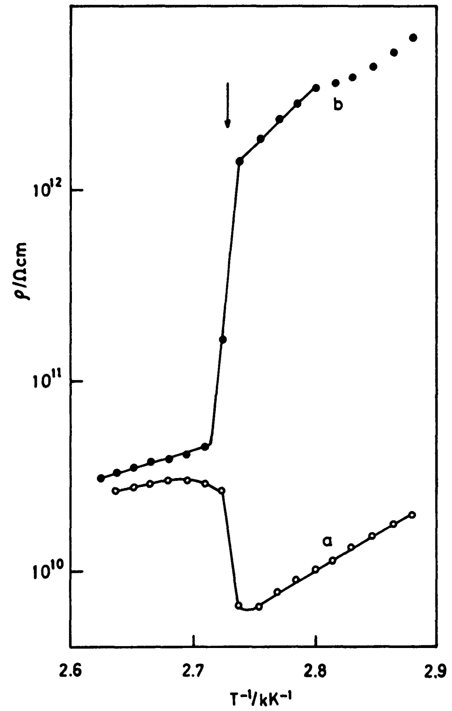

Fig. 2. Electrical resistivity changes of a polycrystalline compaction of fluoranthene-2,4,6-trinitrophenol during (a) the first heating process and (b) the second heating process.

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