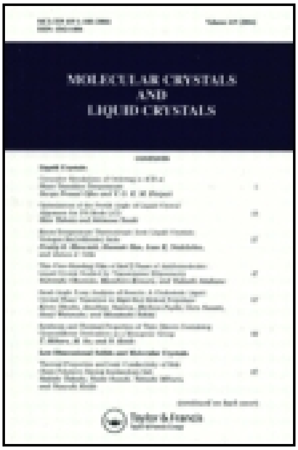

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Kinetic Behaviour of Polymorphic Transition Between Phases α and β of Sublimed p-Dichlorobenzene

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KINETIC BEHAVIOUR OF POLYMORPHIC TRANSITION BETWEEN PHASES α AND β OF SUBLIMED p-DICHLOROBENZENE

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ABSTRACT

Kinetic behaviour of polymorphic transition between phases α and β of sublimed p-dichlorobenzene was drastically altered when the sample was treated at temperatures higher than 70°C(m.p. 53.0°C) for a few hours. Possible interpretations based on the effect of impurities and the effect of mode of aggregation in the sample were suggested.

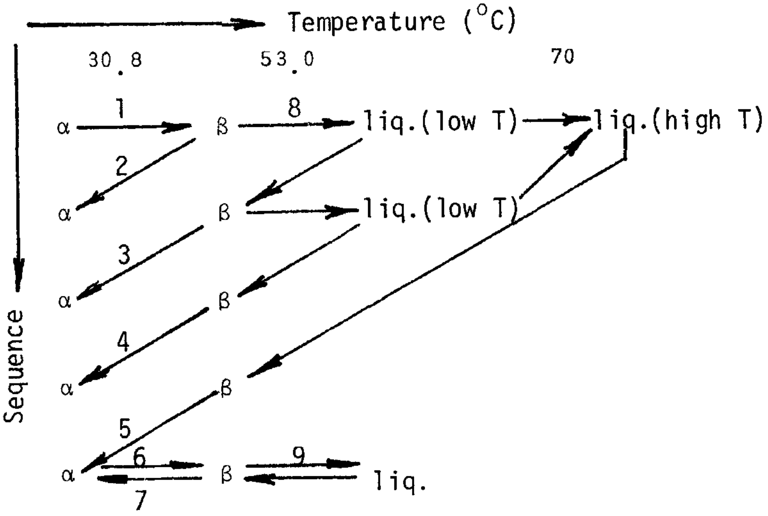
The temperature and the entropy of the transition at about 90 K of the sublimed chloranil have been reported[1] to be lower than those of the sample prepared by recrystallization from benzene solution. This phenomenon was attributed to the fact that the sublimed sample consisted of microdomains 10^3 A° in size.

The present note describes the observation of a peculiar kinetic behaviour of the transition between phases α and β of the sublimed p-dichlorobenzene.

The sample was prepared by subliming p-dichlorobenzene (Matheson Coleman and Bell) in vacuo five times at room temperature onto a glass surface cooled in dry ice bath.

It was stored at room temperature for several months prior to experiments. Raman spectroscopy indicated it was in the α phase. The mole fraction of solid-insoluble impurities was estimated $2\text{x}10^{-4}$ by means of an adiabatic calorimeter[2]. The transitions between phases α and β, as well as melting and freezing were monitored by Raman spectroscopy, dilatometry and DTA technique. A Spex Ramalog Raman spectrometer was used. The temperature of specimen was controlled within ± 2°C. A dilatometer was immersed in a water bath, the temperature of which was controlled within ± 0.05°C. Water was used for dilatometer liquid. A sensitive DTA apparatus was constructed for the present study and described elsewhere[3].

The observed kinetic behaviour of the transition between phases α and β was very complicated, and in particular the occurrence of the change from β to α on cooling was erratic at first sight. After repeated observations, however, it became safe to summarize the results in the diagram below.



The melting of the β phase and the reverse at any stage of sequence in the diagram were ordinary. Process 1, which is the first transition of the sublimed sample from α to β, occurred gradually in the temperature range of about 10°C. On heating constantly at a rate of 1-2°C min^{-1}, DTA runs showed broad peaks barely noticeable even with the sensitive DTA apparatus. At a similar heating rate, the intensity of 27 cm^{-1} peak in Raman spectrum, which is characteristic to the α-phase[4], started to diminish at about 40°C and became zero at about 47°C. This process was so sluggish that the adiabatic calorimetry on a separate sample failed to detect a thermal anomaly. On cooling the β-phase obtained by Process 1 to room temperature, the conversion to phase α (Process 2) did not occur at least a few days. On cooling the sample to room temperature from a melt which had not been heated to higher than 60°C, the conversion from phase β to α (Processes 3 and 4) did not occur at least a day. Once the sample was treated at temperatures higher than 70°C for a few hours, the transition from phase β to α (Process 5) occurred with several hours of induction period at room temperature. In one of the dilatometry runs, the change from β to α at 25.5°C completed within an hour after 4 hours of an induction period. On constantly heating the α phase thus obtained at a rate of 1-2°C min^{-1}, the conversion to phase β (Process 6) occurred, without fail, sharply at about 40°C (∿10°C superheating). DTA gave a sharp peak and the intensity of 27 cm^{-1} peak in Raman spectra dropped sharply. However, when kept at a constant temperature a few degrees lower than 40°C, the rate of transition was slow. In one of dilatometry runs, the rate of growth after nucleation of the β phase was observed to be 1.3% min^{-1} at 36.8°C (6°C higher than the transition point). Process 7 showed the same behaviour as Process 5 and Processes 6 and 7 could be repeated back and forth.

From the results summarized above, the heat treatment of melt at high temperatures (>70°C) for a few hours obviously altered the property of the sublimed sample towards the kinetic behaviour of the transition.

Besides the example of chloranil mentioned above, there have been many other examples in which such secondary effects as strain, impurities, defects, method of preparation, material of sample container, particle size, etc. alter equilibrium properties of mild solid-solid transitions; glass container seemed to stabilize phase Ia of $CC\ell_4$ over the thermodynamically proper Ib[5,6], strain changed the relative stability of two phases in hexamethylethane[7] and in adamantane[8], impurity altered the polymorphism in cesium nitrite[9].

On the other hand, it is kinetic behaviour in solid state (nucleation and growth) that is very sensitively affected by these secondary effects. The present observation porvides one such example.

An important question remains as to which effect causes the phenomena observed here. Impurities is a possible candidate. Indeed, Dworkin et al.[10] did not have as much kinetic problem as the present case in measuring the heat of transition by adiabatic calorimetry, their sample being prepared by recrystallization from ether and the purity being quoted as 99.93 mole %. The heat treatment of the sublimed sample in the present work at high temperature might have caused decomposition and increased impurity content. However, the mole fraction of solid insoluble impurities determined for two separate specimens, one at Process 8 and the other at Process 9 in the diagram above, were $2.0 \pm 0.1 \times 10^{-4}$ and $2.1 \pm 0.1 \times 10^{-4}$ respectively. Hence no unequivocal conclusion could be drawn. Further study with strategically added impurities may be necessary.

Another possible candidate is the effect of mode of molecular aggregation in the sublimed sample. As in sublimed chloranil[1], there may be some long range correlation or lack of it resulting in the formation of micro-domains, which may be completely destroyed only by a prolonged high temperature treatment. Further studies by means of diffuse X-ray and neutron scattering may possibly reveal such feature.

Though no molecular mechanism could be elucidated at this stage it was felt worthwhile to report the present observation, which may have an important bearing with the mode of molecular aggregation in sublimed p-dichlorobenzene.

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