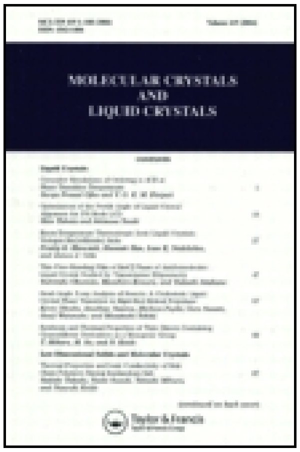

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Polymorphism in Cyclohexanol Reexamined

John R. Green [a] & W. T. Griffith [a]

[a] The University of New Mexico, Albuquerque, New Mexico

Version of record first published: 21 Mar 2007.

To cite this article: John R. Green & W. T. Griffith (1969): Polymorphism in Cyclohexanol Reexamined, Molecular Crystals, 6:1, 23-40

To link to this article: http://dx.doi.org/10.1080/15421406908082951

Molecular Crystals and Liquid Crystals. 1969. Vol. 6, pp. 23–40

Printed in Great Britain

Polymorphism in Cyclohexanol Reexamined‡

JOHN R. GREEN and W. T. GRIFFITH§

The University of New Mexico
Albuquerque
New Mexico

Received September 30, 1968; *in revised form January* 20, 1969

Abstract—Dielectric, visual, and calorimetric observations are brought together to explicate the relations between the four solid forms of cyclohexanol. Rotational form I is stable from the freezing point of 25 °C down to the transition point with non-rotational form III at − 8.3 °C; however, form I can be supercooled well below that temperature. Non-rotational form II has a transition point with form I at − 28.8 °C and is metastable with respect to form III down to about − 64° at which point a transition point occurs between forms II and III. Non-rotational form pre-II has a transition point with I at about − 44°, below which it is metastable with respect to form II. The approximate temperatures for the maximum rates of nucleation are as follows: for I → pre-II, − 87°, for I → III, − 105°, for pre-II → II, − 75°. The approximate temperatures for the maximum growth velocities are as follows: for I → II, − 43°, for I → pre-II, − 60°, for I → III, − 32°. Analysis of I → pre-II growth rates following the theory of continuous growth leads to a transition temperature of − 43.5°, a heat of activation of 9.3 ± 0.5 kcal/mol, and a pre-exponential factor of 5.1×10^9 cm/hr.

1. Introduction

Cyclohexanol has proved to be exceptionally rewarding in studying transformations in the solid state. The many solid forms and the sometimes surprising relations between them constitute a

---

‡ This work was supported in part by the National Science Foundation.

§ NASA Pre-doctoral Trainee 1965–67. Now at Pacific University, Forest Grove, Oregon.

continuing source of information. The fact that form I is a rotational solid‡ with an abnormally high dielectric constant means that dielectric measurements can conveniently be employed to follow transformations between this form and any of the non-rotational forms. The partial transparency of the solid forms makes it possible also to follow the transformations visually in thin layers. The time scales of the transformations are convenient, and the temperatures involved are for the most part obtainable through mechanical refrigeration and can consequently be readily and closely controlled.

The relations between the various solid forms of cyclohexanol have been a source of some confusion in the literature. There have been many studies of various types on solid cyclohexanol and almost all of these, including our own work, have suffered to some extent through inadequate knowledge as to which forms were present. In any such study it would be highly desirable to understand not only which solid form is the stable form at a given temperature, but also to have as much information as possible on the kinetics of transformation between the various forms. Indeed, if any definitive work is to be done regarding the crystal structures or calorimeteric parameters of the non-rotational solid forms, some pre-knowledge regarding stability and kinetics will be necessary.

The existence of at least three solid forms of cyclohexanol has been generally acknowledged. The distinction between the two

---

‡Here we use the term "rotational solid" synonymously with the more common term " plastic crystal " to denote a molecular solid in which the molecules have considerable orientational freedom. On the basis of a particular model that they used to explain the dielectric dispersion in cyclohexanol, Corfield and Davies[1] have claimed that form I of cyclohexanol should not be considered as a " rotator-phase " solid. However, it does possess all of the usual characteristics of rotational solids: a high dielectric constant, a low entropy of fusion, high entropies of transition to the lower temperature forms, and a highly symmetric crystal structure (face-centered cubic). We are of the opinion that none of the current interpretations of the various domains of dielectric dispersion in cyclohexanol are compelling enough to override these other considerations and that form I should still be considered as a rotational solid.

non-rotational forms II and III was first recognized by Crowe and Smyth[2] who introduced the notation used here. Form II is the form which is generally encountered first upon supercooling form I, since II nucleates more readily than III. Form III, however, is stable at higher temperatures than II; III transforms back to I at −8.3 °C, whereas II transforms back to I at −28.8°. This difference in transition points has been the primary and most reliable method of distinguishing these two forms. The free energy diagram of Fig. 6 at the end of this paper indicates the ranges of stability of forms I, II, and III as we now understand them.

In an earlier paper[3] we reported the results of a study on the bulk kinetics of the transformations of cyclohexanol in the solid state by means of dielectric measurements: the rather slow transformations from form I to form III in the temperature range of −20 to −35 °C from but a few nucleation centers, the more rapid transformation from form I to form II at temperatures below −40° from many nucleation centers, and the sharp and rapid transformations from form II to form I at −28.8° and from form III to form I at −8.3°. The I → II and I → III transformations above −60 °C are largely dominated by the kinetics of the growth of forms II and III at the expense of form I. These growth rates have been measured, as well as the growth rates of the II → III transformation between −55 and −28 °C, and are being reported in a separate paper.[4] These two papers provide a reasonably clear picture of the transition kinetics above −60 °C.

Below −60 °C there are some interesting effects which have thus far not been adequately explained. When a sample of cyclohexanol is warmed slowly from liquid nitrogen temperatures, there is a rise in dielectric constant beginning just below −110° and reaching a peak between −98° and −85° depending on the rate of warming. In our first paper we assumed that this effect, first reported by Reinisch,[5] was associated with the transformation from form II to form III. This assumption was incorrect. The only other serious attempt to explain this low temperature behavior was made by Otsubo and Sugawara.[6] These authors suggested that two additional solid forms, which they called pre-II and pre-III, were necessary to explain the results of their thermal studies and X-ray data. The transformations from supercooled form I to both pre-II and pre-III were assumed to occur in the vicinity of −93 °C and the transformations from pre-II or pre-III to the corresponding forms II or III were supposed to occur in the vicinity of −74°. The forms involved were thought to depend on how far the sample was cooled before warming.

In this paper we shall report on dielectric measurements and visual observations that show that all of the presently known facts regarding the low temperature behavior of cyclohexanol can be explained in terms of the single additional form pre-II. We shall discuss the kinetics of the I → pre-II transition and present evidence for a pre-II → I transition point at −44 °C. We shall also discuss the problem of the relative stability of forms II and III. Finally, we shall summarize all that we now know about the phase relations and transformation kinetics in cyclohexanol.

2. Experimental Details

The capacitor used for most of the dielectric work was a three-terminal cylindrical capacitor machined from brass with an inner radius of 1.351 cm, an outer radius of 1.500 cm, and an effective length of 12.65 cm. Both calculations from the geometry and calibration with benzene gave a capacitance of 65 ± 1 pf for the empty capacitor. The capacitor was measured with a General Radio Type 1620-A capacitance bridge, which has a range of useable frequencies from 0.1 to 100 kc/s. The measurement of the bulk rates of transition were made using the two-terminal capacitor and capacitance recording arrangement described in reference 3 and the visual observations were made using the sample vessels described in reference 4. Temperature control was achiveed with either of two environmental chambers, one by General Thermodynamics and the other by Conrad, Inc. Both chambers were capable of cooling to the vicinity of −80 °C by two-stage mechanical refrigeration and to still lower temperatures by use of liquid nitrogen. The chambers controlled to within 0.5 °C for periods of a few days and to even better accuracy for shorter times. Temperatures were measured with copper-constantan thermocouples which were inserted into the hollow center of the cylindrical capacitor, or in the case of the visual observations, were taped to the exterior of the sample vessel. The cyclohexanol was repurified from Eastman Cryoscopic grade by distillation over burnt lime and finally over metallic sodium. Melting points ranged from 24.5° to 25.0 °C.

3. Discussion of Low Temperature Experiments

The first step in studying the low temperature behavior of cyclohexanol was to investigate in detail the dielectric peak in the vicinity of $-90°$ and subsequent drop in the vicinity of -75 °C which were first reported by Reinisch.[5] These features are shown in Fig. 1, which is a plot of dielectric constant as a function of temperature for a sample that had been cooled rapidly to about -120 °C and then warmed at the relatively slow rate of 0.6 °C/min. The measurements were made at 1 kc/s. For this particular rate of warming the dielectric peak appears at $-94°$.

One of the difficulties in unravelling the significance of these effects by dielectric measurements alone is that forms II and III are essentially indistinguishable dielectrically at temperatures below $-40°$. In order to determine what proportion of forms II and III are present it is necessary to run the sample through the II → I transition point at $-28.8°$. At this temperature form II transforms rapidly to form I, which then transforms slowly into form III if growth centers of III are available. The height of the resulting peak in dielectric constant can be used to estimate the relative proportions of forms II and III that were present. However, since we have established that form II will transform directly to form III with appreciable growth rates between $-50°$ and -28 °C, it is imperative that the sample be warmed as rapidly as possible through that temperature range.

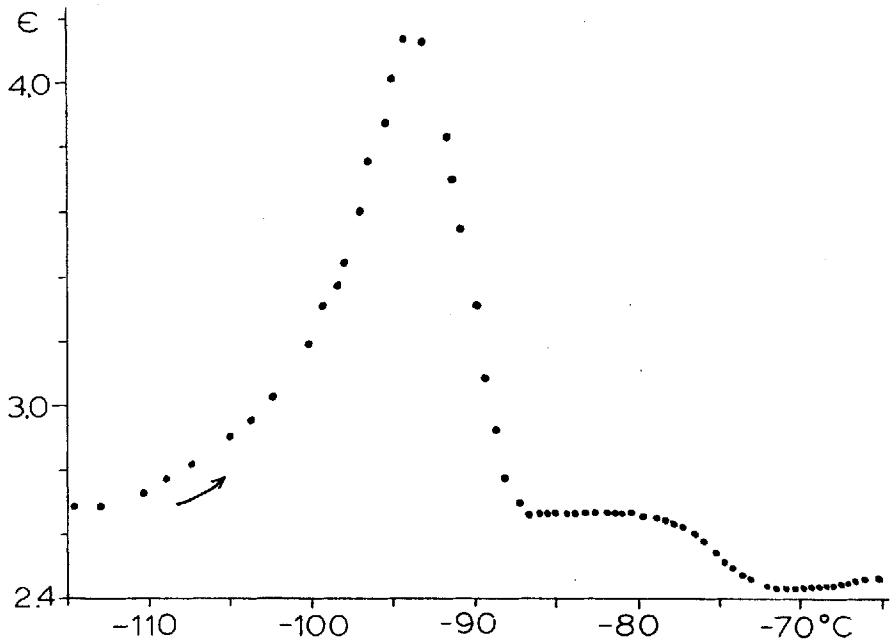

Figure 1. The dielectric constant of a sample of cyclohexanol that was rapidly cooled to −120 °C and then warmed at 0.6 °C/min as a function of temperature.

We have done several experiments in which the sample was cooled with liquid nitrogen and then warmed. The rates of warming were varied, the samples were sometimes held at certain temperatures, and dielectric measurements were made at different frequencies. After each experiment the sample was warmed rapidly through the −28.8° transition and an estimate of the relative proportions of forms II and III obtained. From these experiments the following facts have emerged:

1. The height of the peak in dielectric constant in the vicinity of −90° is extremely frequency dependent, being smaller higher frequencies.
2. The magnitude of the drop in dielectric constant in the vicinity of −75° is quite consistent and is not strongly frequency dependent.

3. The positions of both the peak and the subsequent drop are shifted to higher temperatures when the rate of warming is increased. At very rapid warming rates the two effects tend to coalesce.
4. At −28.8° the greatest amount of form II is found for those runs in which the sample has spent the least time in the vicinity of −100 to −110 °C and conversely the greatest amount of form III is found for runs in which the sample has spent the most time in this temperature range.
5. The peak in the vicinity of −90 °C and the drop in dielectric constant in the vicinity of −75° are always present upon warming from below −100°, but these effects are somewhat smaller in those runs in which the largest amounts of form III are obtained.

Some aspects of the interpretation of these results seem relatively straightforward. When a sample is cooled quickly to −120° or below, it exists mostly as supercooled form I. The dielectric constant at −120° is generally near 2.7 as contrasted with the value of 2.4 regularly displayed by both forms II and III at that temperature. The sample also shows somewhat more dielectric dispersion in this condition than would either II or III. The reason for the relatively small dielectric constant for the rotational form I is that the lowest frequency domain of dielectric dispersion is not activated at these temperatures. It is known that there are two other domains associated with higher frequencies that would account for the dispersion observed.[7] Results for the dielectric dispersion for the domain at lowest frequency are summarized in Fig. 2 from the reports of many workers. By extrapolating only a small amount, we can see that at −90° the critical frequency is about 500 c/s, whereas at −100° it should be well below 100 c/s. Hence the rise in the dielectric constant measured at 1 kc/s in the neighbourhood of −100° as shown in Fig. 1 is clearly caused by the onset of the lowest frequency domain of dielectric dispersion for supercooled form I.

The decline in dielectric constant which begins near −94° in Fig. 1, but can appear anywhere between −96° and −86°

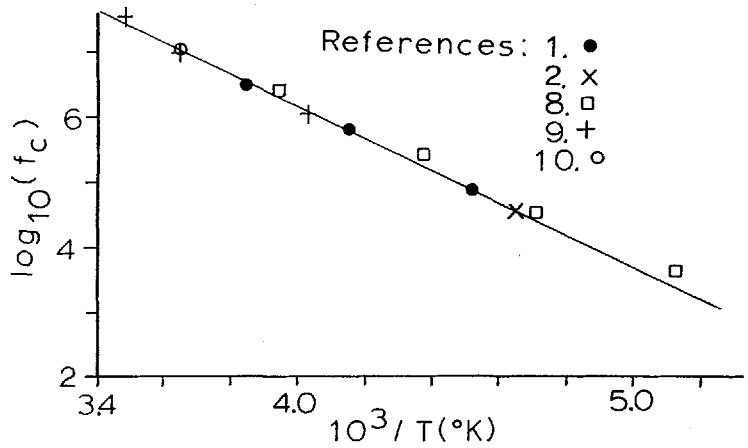

Figure 2. Summary of dielectric relaxation data for cyclohexanol.

depending on the rate of warming, indicates a rather fast transformation to a non-rotational form. This interpretation is consistent with the fact that in this temperature range Otsubo and Sugawara[6] found a thermal minimum indicating an exothermal transformation. The further drop in dielectric constant in the vicinity of −75° corresponds to another exothermal phase transformation and is consistent with the second thermal minimum reported by Otsubo and Sugawara in this region. The exothermal nature of these two transitions is also indicated by our own warming curves.

It is difficult to explain these facts without assuming the existence of at least the transitional form pre-II suggested by Otsubo and Sugawara. Thus the transformation found in the neighborhood of −90° can be interpreted as representing the transformation from supercooled form I to pre-II. The transformation in the neighborhood of −75° would then represent that from pre-II to II. If form pre-II is non-rotational but has a slightly higher dielectric constant than form II, then this interpretation would explain the dielectric data.

We have been able to find no evidence that requires the existence of the additional form pre-III which was also suggested by Otsubo and Sugawara. Their reason for postulating such a form seems to have been that when they cooled their sample below −100°, they observed the same thermal minima at −93° and −74° upon warming as they did when the sample had not been cooled below −100°. On the other hand, the sample which had been cooled below −100° showed a large proportion of form III present at the −28° transition point, whereas the sample which had not been cooled below −100° did not show much form III. From these results they concluded that for the case where the sample had been cooled below −100°, the two thermal minima must represent the transformations I → pre-III and pre-III → III since form III was the end product.

The results of our dielectric experiments are in essential agreement with the experimental observations of Otsubo and Sugawara regarding the proportions of forms II and III which result in the two cases mentioned above. However, we have been able to establish through visual observations that there is a maximum in the nucleation rate of form III from I in the vicinity of −105°. Since the growth rate of III from I should be negligible at this temperature there would usually still be a large proportion of form I present to go through the I → pre-II and pre-II → II transformations. Our measurements of growth velocities[4] have established, however, that form III will grow from II with significant rates between −50° and −28°. Hence if there are enough growth centers present, the sample could transform completely to form III during the warming process. These facts together with the assumed existence of the form pre-II seem adequate to explain all of the dielectric results listed above as well as the thermal data of Otsubo and Sugawara.

4. Pre-II → I Transition Point

Form pre-II is apparently a metastable, transitional form between forms I and II. If so, there should be a transition point for pre-II → I somewhere below the II → I transition point of −28.8°. However, if this transition point lies above −75° it would be difficult to observe because of the rapid transformation of pre-II to II in that vicinity. We had hitherto not observed any irregularities in the dielectric behavior between −70° and −28.8°, but in the dielectric curve reported by Fujimura and Kamiyoshi[11] for a sample being heated from −150° there is a small unexplained peak at about −45°. An additional peculiarity of their work, the relative sluggishness of the transformations to non-rotational forms, suggests, in view of our own experience, a sample with a rather high water content. If this sluggishness applied to the pre-II → II transformation as well, then there may have been enough pre-II present to produce a noticeable pre-II → I transformation at the presumed transition point of −45°.

To test these surmises, we made two runs using a sample of cyclohexanol which had absorbed enough water to lower its melting point to 5°—well below the melting point of 25° for a pure sample. In the first run the sample was cooled to about −76° and held there for 17 hours before being warmed rapidly through −45°. In the second run the sample was held at −76° for only 5 hours before being warmed through −45°. The results of the dielectric measurements are shown in Fig. 3. The lower dielectric

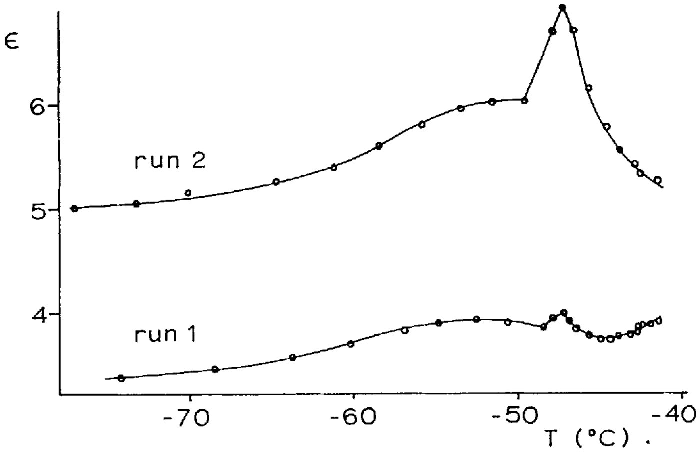

Figure 3. The dielectric constant of a sample of impure cyclohexanol (m.p. 5 °C) being warmed through the transition point in the vicinity of − 45 °C for two different thermal histories.

constant in the first run indicates that most of the sample had transformed to II, but even so the two runs show the same general features. The gradual rise in dielectric constant with temperature is probably due mostly to a rise in the dielectric constant of pre-II as its transition point to I is approached. The slight decrease in the vicinity of −52° can be attributed to the pre-II → II transformation, and the peak at −47° to the pre-II → I transition followed by a rapid I → II transformation. The transition points for II → I and III → I for the impure sample were −31° and −11° respectively; these are roughly 3° lower than for pure samples. Assuming that all transition points are affected in the same way, we can then estimate a pre-II → I transition point of −44° for a pure sample.

Further support for a pre-II → I transition point in this vicinity is found in the visual observations. We had measured growth velocities for a transformation which we had originally designated as the " dark mode " of the I → II transformation.[4] This transformation proceeds with considerably larger growth velocities than the normal I → II growth, and the bulk appearance of this growth is usually more opaque than the normal growth. This mode of growth is only observed below −45°. If it is started growing below −45°, where both normal and the dark mode will grow, and then warmed to above −45°, the dark mode will revert to the growth velocities and appearance characteristic of normal I → II growth. The closeness of this temperature to that of our estimate for the pre-II → I transition point suggested that this mode of growth represents the transformation I → pre-II → II. Additional visual observations at lower temperatures have indicated that the dark mode of growth does indeed involve the same form that is responsible for the dielectric peak and thermal minimum in the vicinity of −90°.

5. Kinetics of the I → pre-II Transformation

The " dark mode " growth velocities which we had measured were apparently characteristic of the I → pre-II transformation;

the kinetics of the pre-II → II transformation in this temperature range are less clear. We have extended the measurements of I → pre-II growth velocities beyond those reported in reference 4. The results, which are plotted in Fig. 4, show a maximum at about −60° followed by a rather steep decline. We have analyzed these data following the theory of continuous growth.[4] The latent heat of transformation L is not known, but it must be considerably less than the value of 2 kcal/mol for the II → I transformation. Fortunately, this is not a sensitive parameter, so we have simply taken the value of 1 kcal/mol for it. The best fit is obtained for a transition temperature $T_0 = -43.5°$ with an enthalpy of activation $\Delta H^* = 9.3 \pm 0.5$ kcal/mol and a pre-exponential factor $A = 5 \times 10^9$ cm/hr. The smooth curve in Fig. 4 is a plot of $A \exp(-\Delta H^*/RT)[1 - \exp(-\Delta G/RT)]$, where $\Delta G = L(T - T_0)/T$. The enthalpy of activation and the pre-exponential factor are quite similar to those obtained for the I → III transformation.[4]

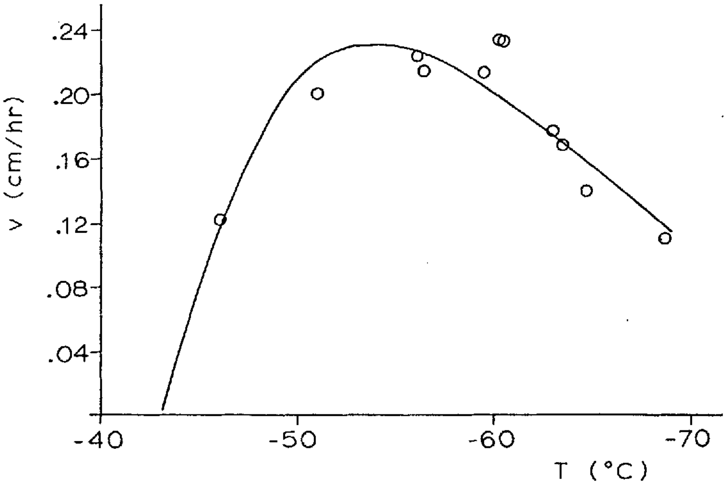

Figure 4. Growth rates for the I → pre-II transformation. The smooth curve is the result of analysis following the theory of continuous growth.

We have also extended to lower temperatures the measurement of the bulk rates of transformation which were reported in reference 3. The results of these measurements are shown in Fig. 5, where we have plotted the reciprocal of the half-time of the transformation as a function of temperature. The half-time is defined as the time taken for the dielectric constant to drop by half of its total change. The samples were cooled rapidly with liquid nitrogen to the desired temperature of transformation and the time $t = 0$ was taken as the time at which this temperature was reached. The maximum shown by the data between $-85°$ and $-90°$ is consistent with our interpretation of a rapid I → pre-II transformation in this vicinity. The slight hump in the curve in the neighborhood of $-60°$ can be attributed to the maximum in the growth velocity of I → pre-II at that temperature. At lower temperatures visual observations confirm that the rate of transformation is dominated by the rate of nucleation. Hence

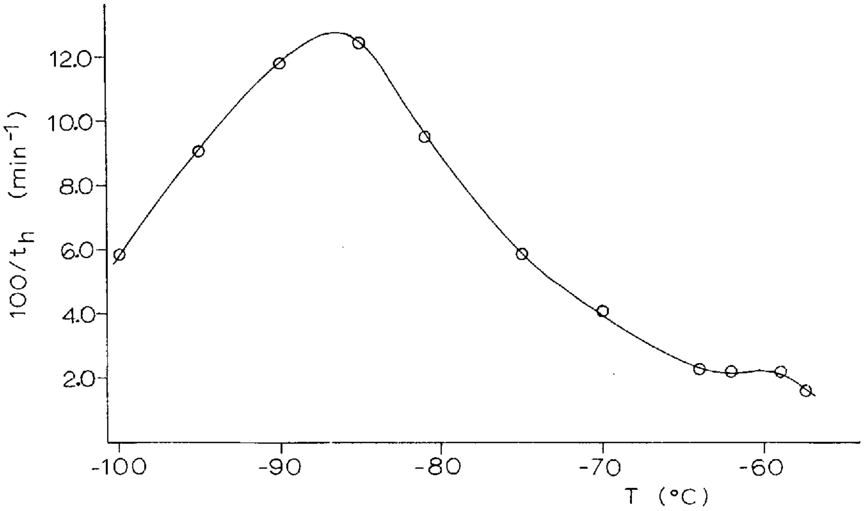

Figure 5. The reciprocal of the half-time for the bulk rates of transformation of cyclohexanol from rotational to non-rotational forms as a function of temperature.

the maximum in the vicinity of − 90° is representative of a maximum in the rate of nucleation of form pre-II from I.

Visual observations have generally confirmed the features indicated by the thermal and dielectric measurements and have often provided considerable insight on the nature of the transformation process. Form I remains transparent even when supercooled to as low as − 120°. Pre-II can be observed to form as translucent growths that destroy the polarization of the incident light. In the vicinity of − 90° the nucleation of pre-II is so extensive that individual growth centers are difficult to distinguish; above − 80°, on the other hand, they can be readily distinguished under low magnification. The transformation from pre-II to II is seen as a rather rapid darkening of the sample, often accompanied by the formation of many tiny cracks. The formation of the cracks would indicate that there is a significant difference in density between forms II and pre-II. We have been unable to distinguish individual growth centers for the pre-II → II transformation and thus we are not sure whether the transformation in the vicinity of − 75° represents rapid nucleation or rapid growth of form II. However, the very general nature of the transformation would suggest that it is a nucleation phenomenon. Also the slight decrease in dielectric constant shown in the curves of Fig. 3 would indicate that the maximum in the pre-II → II growth rate may fall in the neighborhood of the pre-II → I transition point.

6. The II–III Transition Point

From the time that Crowe and Smyth[2] first established that there were at least two non-rotational forms, II and III, III has been assumed to be the ultimately stable form. We at first took this view; however, our data for the growth velocities of the II → III transformation between − 55° and − 28.8° suggested that form II was superheated rather than supercooled in this temperature range.[4] A best fit of these data to the theory of continuous growth was obtained for a II-III transition point of

− 64°, although other, almost equally good fits were possible for transition points near − 11°.

Attempts to observe the reverse transformation from III to II below − 64° yielded null results. Calculations using the parameters obtained from the fit to the II → III data indicate that the maximum growth velocity to be expected for the III → II transformation should indeed be too small to be observable. Of the other types of experiment which might resolve the issue, calorimetric measurements would be the most definite, but we are not equipped to perform accurate calorimetric work. However, in order to determine simply whether the transition point is above or below the temperature range of the observed II → III transformation, it is sufficient to determine whether this transformation is exothermic or endothermic. To this end we have done a rather crude thermal experiment employing two thermocouples, one inside and the other outside a large sample of cyclohexanol. The sample was cooled rapidly to the vicinity of − 105° and then allowed to warm slowly while the temperatures inside and out were recorded. In the vicinity of − 105° considerable nucleation of form III will occur and these nuclei will grow with gradually increasing velocities between − 55° and − 28°. This transformation was observable as a slight decrease in the warming rate of the interior thermocouple relative to the exterior one in the vicinity of − 35°. Although the effect was small it did not seem to definitely indicate that the II → III transformation is endothermal.

The endothermal nature of the II → III transformation would imply that form II is the form which is ultimately stable at low temperatures. In addition to our own growth velocity data, there have been other indications that this is the case. The heat of transition of 2.0–2.1 kcal/mol estimated by Otsubo and Sugawara for the II → I transformation yields a slightly higher entropy of transition for II → I than that of the III → I transformation. Also, the velocity of ultrasound data, reported by Green and Scheie[12] suggest that form II is more tightly bound than form III.

7. Conclusions and Summary of Phase Relations

For any transformation from a supercooled phase to a form more stable at lower temperature, it is expected that there will be a maximum in the growth velocity curve at some temperature below the equilibrium transition point T_0 and also a maximum in the nucleation rate at some lower temperature. In this paper we have presented evidence for the existence of the phase pre-II and have established its transition point back to I and the temperatures for maximum rates of nucleation and growth. These results are summarized in Table 1 along with similar data for the other transformations in cyclohexanol that we have studied.

Table 1 Importnat parameters for transformations between various forms of solid cyclohexanol. The reverse transformations occur sharply and, quickly at the transition points except for the II → III transformation, whose behavior is characteristic of a superheated transformation.

Transformation	Transition Point (°C)	Temperature of Maximum Growth Velodity (°C)	Temperature of Maximum Nucleation Rate (°C) (°C)
I → II	– 28.8	– 43	?
I → pre-II	– 44	– 60	– 87
I → III	– 8.3	– 32	– 105
III → II	– 64	not observable	?
pre-II → II	?	?	– 75

As is indicated by the question marks there are still some points that remain to be clarified. Some of these may not be experimentally accessible. For example, it is possible that there is a maximum in the rate of I → II nucleation somewhere between – 60° and – 90°, but that it is completely overshadowed by the much faster I → pre-II nucleation. Other transformations such as III → II or pre-II → III may be just too slow to detect experimentally.

To clarify further our present picture of the phase relations in solid cyclohexanol we have plotted a hypothetical diagram of free energy against temperature in Fig. 6. The curves for forms I and III are based on numerical integration of the heat capacity data of Kelley.[13] The curve for form II has been sketched as shown on the basis of its transition points with forms I and III. The II → I transition point is firmly established but the II → III transition point of − 64° may be considerably in error. Finally, the curve for pre-II has been sketched as shown on the basis of its transition point back to I and the fact that pre-II has a larger entropy than form II as indicated by the exothermic nature of the pre-II → II transformation. Within these limits the slope of the pre-II curve is arbitrary.

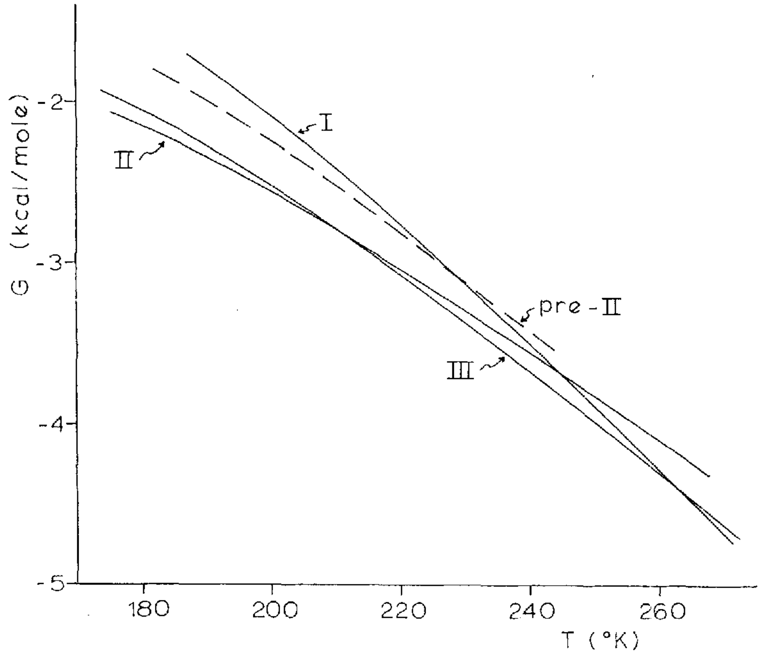

Figure 6. Hypothetical free energy curves for the various solid forms of cyclohexanol.

Although we have not by any means exhausted the wealth of information that can be gained by dielectric studies and visual observation on solid cyclohexanol, probably the most pressing need at this point is for good calorimetric data on forms II and pre-II. It would also be highly desirable to know the crystal structures of all three of the non-rotational forms II, III, and pre-II. These would be difficult to obtain, but would be invaluable in the interpretation of the data we have accumulated on the kinetics of the transformations.

REFERENCES

1. Corfield, G. and Davies, M., *Trans. Faraday Soc.* **60**, 10 (1964).
2. Crowe, R. W. and Smyth, C. P., *J. Amer. Chem. Soc.* **73**, 5406 (1951).
3. Green, J. R. and Griffith, W. T., *J. Phys. Chem. Solids* **26**, 631 (1965).
4. Green, J. R. and Griffith, W. T., to be published *J. Crystal Growth.*
5. Reinisch, L., *Compt. Rend.* **237**, 50 (1953).
6. Otsubo, A. and Sugawara, T., *Scientific Reports of the Research Institute, Tohoku University* **A–7**, 583 (1955).
7. Garg, S. K. and Smyth, C. P., *J. Chem. Phys.* **46**, 373 (1967).
8. Meakins, R. J., *Trans. Faraday Soc.* **58**, 1962 (1962).
9. Reinisch, L., *Compt. Rend.* **237**, 564 (1953).
10. Arnoult, R., Lebrun, A. and Boullet, C., *Archives des Sciences* **9**, 44 (1956).
11. Fujimura, T. and Kamiyoshi, K., *Scientific Reports of the Research Institute,* Tohoku University **A–13**, 320 (1961).
12. Green, J. R. and Scheie, C. E., *J. Phys. Chem. Solids* **28**, 383 (1967).
13. Kelley, K. K., *J. Amer. Chem. Soc.* **51**, 1400 (1929).