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A STUDY OF THE POLYMORPHIC $\alpha \rightleftarrows \beta$ TRANSITION IN MONOCRYSTALLINE PARA-DICHLOROBENZENE

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A new approach to the measurement of the polymorphic transformation rates in para-dichlorobenzene is proposed on the basis of a study of the regularities of the polymorphic transformation. It is shown that the rate of transition of a unit volume to a different phase of a unit volume or unit area of the crystal is not a physical characteristic of the process under consideration. The conditions to be met in an "ideal" experiment for measuring the transformation rates are formulated. In the experimental part of the work the velocity V of polymorphic transformation of para-dichlorobenzene is measured as a function of two factors: the number of "single crystal—single crystal" type transformations in the given crystal, n, and the temperature. A peak in the V(n) curve and relaxation of this property depending on the duration of "rest" of the crystal have been observed. The $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ activation energies are computed from the V(T) curves; the corresponding values are $E_1 = 17.4 \pm 2.5$ and $E_2 = 17.1 \pm 2.5$ kcal/mole.

INTRODUCTION

THIS study is a continuation of our investigations of the mechanism of polymorphic transitions in organic molecular crystals. We have shown[1,2] that:

1) The polymorphic "single crystal-single crystal" transition in p-dichlorobenzene occurs by growth of a faceted single crystal within the solid monocrystalline medium of the unstable phase.

2) Not only does no crystallographic relation exist between the lattice orientations of the growing and the original phases of p-dichlorobenzene, but no regular relation at all: the single crystal of the original phase acts like an "isotropic" medium for the new growing crystal.

3) In spite of the arbitrary lattice orientation of the new phase, it often manifests a phenomenon of "memory" of its previous orientation, which is explained by the preservation of potential nuclei in the defect sites of the crystal.

4) The transitions may be monocentric ("single crystal-single crystal") or polycentric. The difference between the "single crystal-single crystal" and "single crystal-polycrystal" transitions (abbreviated: "s-s" and "s-p") involves only the conditions determining the number of crystallization centers produced.

Attempts have previously been made to measure rates of polymorphic transition in p-dichlorobenzene,[3,4] but the data presented above compel us to examine this problem anew.

FACTORS AFFECTING THE RATE OF POLYMORPHIC TRANSITION. MORE PRECISE DEFINITION OF THE CONCEPT OF RATE OF POLYMORPHIC TRANSITION

Our observations (performed mainly on p-dichlorobenzene) point out the great resemblance between the growth of crystals from a single-crystal medium in a polymorphic transition and the growth of crystals from liquid and gaseous media. This is indicated by the following facts: 1) the faceting of a crystal growing from a solid medium becomes more perfect when the growth process occurs more slowly; 2) the lattice orientation of the crystalline medium apparently exerts no effect on the growth of the crystal of the new phase; 3) the growing crystal always tends to acquire a convex outer boundary, i.e., it shows a tendency toward a minimum free surface energy; 4) the frequently-observed phenomenon of delayed transition (supercooling or superheating) shows the same nature as the phenomenon of supercooling a solution: it is explained by the absence of a sufficient number of formed crystallization centers.

All that has been said implies that each face of the growing crystal of the new phase has its own rate of polymorphic transition, a fact that had never before been taken into account. In the literature, one usually makes a measurement of the rate of motion of "some" phase boundary or even measures the volume rate of transition. Only Lemanceau and Clement [4] have measured the rate of movement of linear boundaries between the α and β phases of p-dichlorobenzene and noted that the rate depends on the crystallographic directions. However, bearing in mind the arbitrary lattice orientation of the crystal of the new phase, we should specify more exactly that the rate of transition depends on the crystallographic directions of the growing crystal, but not of the crystalline medium, as was implied in the cited study.

The greater the transparency and perfection of faces of the original single crystal, the greater is the probability that it will show an α-β transition of the "s-s" type. The occurrence of such a transition requires that only one growth center of the new phase must arise and develop within the volume of the original crystal. However, monocentric transitions are far from universal, and more often they prove to be polycentric. The latter are of two types.

1. Several independent crystallization centers of the new phase arise simultaneously (or nearly so) at different points of the original crystal. Faceted single crystals of differing lattice orientations grow from these centers. Consequently, the original single crystal is transformed into the corresponding number of crystal blocks of the new phase, having random mutual orientations. The crystal remains fully monolithic. Later on, one can obtain a single crystal anew from such a "polycrystal" by polymorphic transition.

2. The polymorphic-transition process is highly unorganized in form. A formless but single phase boundary is propagated through the crystal. The crystal loses its transparency behind the boundary. Laue patterns show that the crystal is transformed into a large number of randomly oriented blocks. Sometimes one can note a slight distortion of the external faces of the crystal; apparently its monolithic nature has been destroyed. In any case, one can no longer get back a single crystal from it by polymorphic transition. We may assume that the stresses and defects, in "running" ahead of such a formless phase boundary, facilitate the formation at these sites of new crystallization centers. Thus the process acquires, as it were, a "wave" nature. Naturally, the rate of such a process can differ greatly from that of growth of a single-crystal face, and can depend on the temperature in a different way.

The important factors affecting the rate of polymorphic transition are the internal stress field of the crystal and its defect content. It is precisely for these reasons that one often observes non-uniform motion of the growing face of a crystal of the new phase while the temperature remains constant. Thus, naturally, the transition rate also depends on the prior history of the crystal; in particular, the experimental section of this article shows this quite evidently.

Thus we arrive at the conclusion that the very concept of the rate of a polymorphic transition must be made still more precise. The purpose of measuring the rate of a polymorphic transition is to elucidate the mechanism of this transformation on the molecular level. Hence, in setting up an experiment we must eliminate as far as possible external factors that affect the process under consideration and are difficult to take into account. In other words, the measured velocity must be a physical characteristic of the polymorphic-transition mechanism in the "ideal" crystal.

First of all, this means that all cases of polycentric transition are excluded from study here. It seems evident that polycentric transitions transform the crystal into the new phase much faster than monocentric ones do, other conditions being equal. This makes it necessary to limit the field of study to monocentric "s-s" transitions. Further, we must take into account the fact that two different methods of measuring the rate of transition are found in the literature. In some cases, the linear velocity of movement of the phase boundary has been measured, and in others, the volume rate of transition. The question arises hereby of which of the mentioned rates is the more valid physical characteristic of the process under discussion. This question is answered by Fig. 1, which illustrates the fact that the volume transition rate is not an unambiguous quantity, since it depends on the site of origin and the orientation of the nucleus of the new phase, and also on the dimensions and form of the original crystal. Hence one must measure the linear, rather than the volume transition rate, i.e., the linear velocity of growth of the (hkl) face of the single crystal of the new phase in a direction normal to this face.

In summary, let us enumerate the conditions for an "ideal" design of an experiment to measure the rate of a polymorphic transition:

1) The original single crystal must be free from stresses and defects.

2) The transition must be monocentric, i.e., of

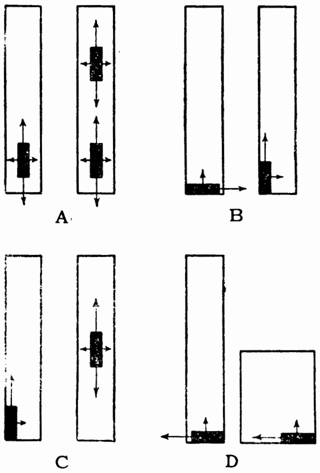

FIG. 1. Dependence of the volume rate of a polymorphic transition on various chance factors: A – on the number of crystallization centers of the new phase produced, B – on the orientation of the nucleus of the single crystal of the new phase, C – on the site at which this nucleus appears, D – on the shape of the original crystal.

the "single crystal-single crystal" type.

3) The quantities to be measured are the linear velocities V_n^{hkl} of growth or the (hk$l$) faces of the new phase in the direction of the normal n to each face. One must assign to each measured velocity the indices of the face whose growth is being measured.

The cited conditions help us to avoid a number of errors in designing an experiment, and in getting a true picture of how much an actual experiment deviates from the ideal. What we have said is confirmed by three examples.

1. One should not use crystals enclosed in the glass tube in which they were grown as objects for measuring transition rates, since: a) the differences in the expansion coefficient of the glass tube and the crystal will create internal stresses in the latter; b) internal stresses can be produced in the crystal by the volume change of the crystal during the polymorphic transition; c) the walls of the tube are a source of crystallization centers of the new phase, and the process cannot be considered monocentric.

2. The usual way of measuring the polymorphic-transition rate is to measure the velocity of movement of some line of separation of the two phases across the surface of the crystal. However, here one does not take into account the following two facts: a) the line of separation of the phases must be strictly linear, since this is the only guarantee of the presence of a monocentric transition, rather than a polycentric one; and b) even when the previous condition is obeyed, and the velocity (V_{meas}) is measured normal to the

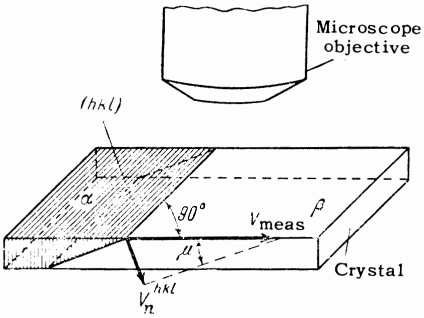

FIG. 2

line of separation of the phases, this velocity will exceed the sought V_n^{hkl} by a factor of $1/\sin\mu$, where μ is the angle of inclination of the growing face (hk$l$) to the surface of the crystal (see Fig. 2).

3. The literature contains studies on the measurement of the rate of transition into a new polymorphic modification of an area of the surface of a crystal in the field of view of a microscope. The methodological error of such an experimental design is evident from the previous discussion.

EXPERIMENTAL SECTION

At present we are not in a position to satisfy fully the idealized conditions formulated above, if only because we do not have completely defect-free crystals, and do not have a method of indexing the faces of the growing crystal of the new polymorphic modification, etc. Besides, we consider the results of the measurements given below to be very crude, and subject to further refinement.

An essential point in the experimental method described below, which we used to measure the rate of polymorphic transition in p-dichlorobenzene, is the fact that we were able to bring about "s-s" transitions in one and the same crystal, as follows:

$$\begin{array}{lcccccccccccc} & \alpha & \to & \beta & \to & \alpha & \to & \beta & \to & \alpha & \to & \beta & \to \ldots \\ n = & 1 & & 2 & & 3 & & 4 & & 5 & & 6 & \ldots \end{array},$$

where n, the ordinal number of the transition, sometimes was as large as 20–30. Qualitative observations showed that V depends on n. Hence we decided to measure V not only as a function of the temperature T, but also as a function of n.

The idea of the experiment consisted in the following. One repeatedly brings about "s-s" transitions from the α-form to the β-form and back in a crystal of acicular or elongated shape, and each time measures the rate of transition of the linear phase-separation boundary. Here one takes care that the absolute value $|\delta| = |T - T_0|$ (where T is the temperature of the transition, while T_0 is the phase-equilibrium temperature) is the same for all n. These measurements are performed repeatedly: for identical δ values on several crystals, and all of this repeated for different δ values. The treatment of this experimental material permits one to obtain the functions V(n), V(T), and the necessary statistics.

The practical difficulties of carrying out these experiments are very great, but not insurmountable. Not nearly every crystal shows an "s-s" transition of the necessary quality, and among the selected crystals, not nearly every one can withstand the necessary number of transitions without changing the indices of the growing face or undergoing an "s-p" transition, whereupon one must often terminate the measurements without completing the experiment.

The measurements are made with two polarizing microscopes supplied with Boetius hot stages and eyepiece reticles. One of the stages is maintained at a constant temperature of $T_1 = T_0 + \delta$, and the other at $T_2 = T_0 - \delta$.

The chosen single crystal (usually of dimensions 1.5—3 mm) is placed in a cell containing glycerol (Fig. 3). The crystal rests on the bottom of the cell, which is a cover glass. The glycerol reliably protects the crystal from sublimation, and acts as a medium to improve heat transfer.

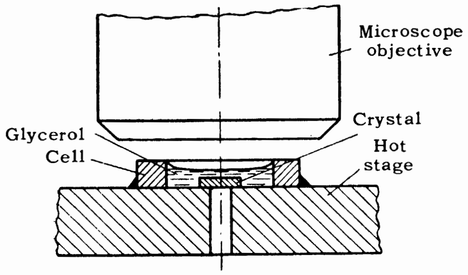

FIG. 3. Specimen in a glycerol bath on the hot stage of the microscope.

One provisionally picks out a region 1 mm long in the middle of the specimen with the eyepiece reticle, and measures the time for the phase boundary to pass across it. Both of the side regions of the crystal act as auxiliaries. The crystal is heated to the temperature of onset of the $\alpha \rightarrow \beta$ transition (which is always higher than T_0). If it turns out that the transition is "s-s", and it takes place at one of the ends of the specimen, the cell is placed on the stage at temperature T_1. After a certain time necessary for the temperature of the specimen and the stage to become equal and the phase boundary to reach the graduation line of the eyepiece reticle marking the beginning of the main region, a stopwatch is started. After the phase boundary has traveled 1 mm, the stopwatch is stopped. The specimen is transferred to the other microscope, with care taken that the transformation doesn't reach the end. The latter is necessary in order that for all values of n measurements be made on the same (hk*l*) growth faces of the α- and β-crystals. When the crystal reaches the temperature T_2 and the phase boundary reaches the graduation mark indicating the beginning of the main region 1 mm long, the rate $V_{\beta \rightarrow \alpha}$ is measured. This procedure of shifting the phase boundary back and forth is repeated many times.

The results of the measurements (of about twenty crystals) reveal the following properties in the crystals:

1. The V(n) curves show a maximum (see Fig. 4). The curves for $V_{\alpha \rightarrow \beta}(n)$ and $V_{\beta \rightarrow \alpha}(n)$ obtained in a single experiment vary in parallel, as a rule.

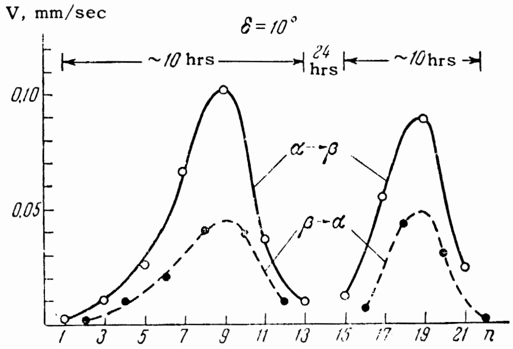

FIG. 4. A typical example showing the relation of the rate of transition in p-dichlorobenzene to the mumber n of "s–s" transitions undergone by one of the studied crystals. The existence of two effects is shown: the existence of a maximum, and relaxation.

2. Relaxation takes place during a period of "rest" of the crystal. This is expressed in a partial or complete restoration of the original transition rate and of the ability to exhibit a maximum on the V(n) curve. The relaxation is the more complete, the smaller n is and the longer the "rest" period.

3. With sufficiently large n (~20 or greater), one can arrive at a situation where V = 0 when $T \neq T_0$.

Figure 5 shows a photograph of an acicular crystal of paradichlorobenzene in which the boundary between the α- and β-phases has been shifted back and forth by temperature variation. As a result of these manipulations, the phase

Mean rates $\overline{V}(\delta)$ and $\overline{\overline{V}}(\delta)$

	$\alpha\to\beta$				$\beta\to\alpha$			
	$\delta=+2$	$\delta=+5$	$\delta=+11$	$\delta=+15$	$-\delta=-2$	$-\delta=-5$	$-\delta=-11$	$-\delta=-5$
$\overline{V}$, mm/sec	$6\cdot10^{-4}$ $7.3\cdot10^{-4}$ $9.7\cdot10^{-4}$ $11.3\cdot10^{-4}$	$5\cdot10^{-3}$ $4.6\cdot10^{-3}$ $6.7\cdot10^{-3}$	$5\cdot10^{-2}$ $2.1\cdot10^{-2}$ $11.7\cdot10^{-2}$ $3.3\cdot10^{-2}$ $3.9\cdot10^{-2}$ $3.0\cdot10^{-2}$	$7.3\cdot10^{-2}$ $4.5\cdot10^{-2}$ $9.2\cdot10^{-2}$ $6.8\cdot10^{-2}$	$3\cdot10^{-4}$ $2.4\cdot10^{-4}$ $6\cdot10^{-4}$ $4\cdot10^{-4}$	$1.4\cdot10^{-3}$ $1.7\cdot10^{-3}$ $1.9\cdot10^{-3}$	$0.9\cdot10^{-2}$ $0.5\cdot10^{-2}$ $2.8\cdot10^{-2}$ $1.2\cdot10^{-2}$ $1.1\cdot10^{-2}$ $1.1\cdot10^{-2}$	$0.33\cdot10^{-2}$ $0.23\cdot10^{-2}$ $0.25\cdot10^{-2}$ $1.4\cdot10^{-2}$
$\overline{\overline{V}}$, mm/sec	$8.6\cdot10^{-4}$	$5.4\cdot10^{-3}$	$4.8\cdot10^{-2}$	$7.0\cdot10^{-2}$	$3.85\cdot10^{-4}$	$1.7\cdot10^{-3}$	$1.3\cdot10^{-2}$	$0.55\cdot10^{-2}$

FIG. 5

boundary became fixed and insensitive to variations in the temperature of the crystal. In this state, the crystal was preserved for weeks at room temperature, which is 10° lower than T_0. Relaxation proceeded very slowly.

The experimental data obtained were subjected to further treatment. Curves of $V_{\alpha\to\beta}(n)$ and $V_{\beta\to\alpha}(n)$ like those in Fig. 4 were plotted for all the crystals and integrated graphically with a planimeter. Thus the values $\overline{V}_{\alpha\to\beta}$ and $\overline{V}_{\beta\to\alpha}$ averaged over n were calculated:

$$\overline{V}=\frac{1}{\Delta n}\int\limits_{\Delta n} V dn.$$

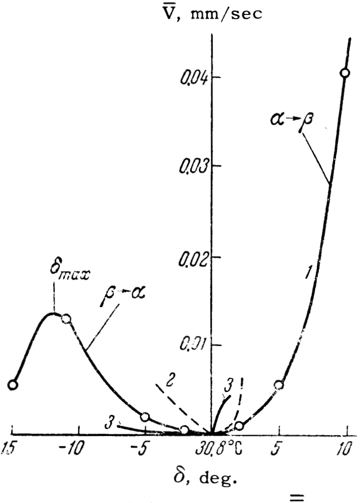

FIG. 6. The relation of the mean rate $\overline{\overline{V}}$ of the polymorphic transition to the temperature; $\delta = T - T_0$, where T is the transition temperature and T_0 is the phase-equilibrium temperature. All of the values of $\overline{\overline{V}}$ from which curve 1 was drawn are too high by a factor of about 1.5–2 because of the inclination factor, the nature of which can be seen from Fig. 2. For comparison, the V(T) curves taken from other authors are shown: 2 (see [3]) and curve 3 (see [4]).

These values were averaged again, this time over all the crystals having the same value of δ. The doubly-averaged values of the rates were denoted by $\overline{\overline{V}}$. The results of the two averagings are given in the table. Figure 6 shows the curve $\overline{\overline{V}}(\delta)$, which is compared with the curves from the studies of other authors.[3,4] Figure 7 shows the curve

$$\eta(\delta) = |\overline{\overline{V}}_{\alpha\to\beta}(\delta)| \,/\, |\overline{\overline{V}}_{\beta\to\alpha}(\delta)|.$$

DISCUSSION OF RESULTS

1. The existence of a maximum on the V(n) curve. Relaxation. We can as yet say very little on the nature of these phenomena. The existence of a maximum on the V(n) curve indicates the existence of at least two competing factors. The displacement of the phase boundary through the volume of the crystal has a certain resemblance to the process of zone melting. Possibly the admixture of impurities, stresses, and dislocations is "forced out" of the crystal. As for the impurities, the fact of relaxation denies that they participate in the appearance of the maximum on the V(n) curve.

Any explanation of the cited effect must be

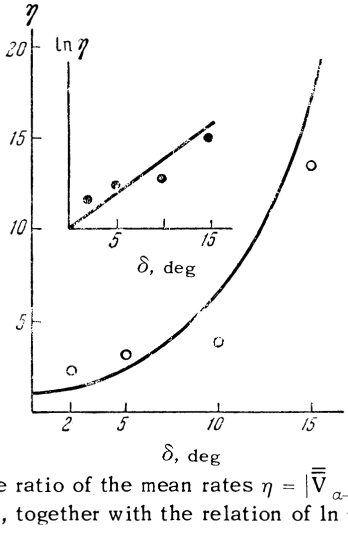

FIG. 7. The ratio of the mean rates $\eta = |\overline{\overline{V}}_{\alpha\to\beta}| \,/\, |\overline{\overline{V}}_{\beta\to\alpha}|$ as a function of δ, together with the relation of ln η to δ.

compatible with the fact that it does not depend on which transition is taking place ($\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$), toward which side the phase boundary is being shifted, and which (hk*l*) indices the growth face has.[1)]

The existence of the V(n) relation again confirms how cautiously one must treat the variation of the rate of a polymorphic transition. Quite indubitably, the latter is determined both by the structures of the ideal crystals of the two modifications (which in turn determine the values of the free energies of the phases and the "true" activation energies), and by the defect content. However, the latter depends on the prior history of the crystal, and hence, a random experiment will result in practically nothing.

2. The temperature-dependence of the transition rate. Activation energy. We can arrive at an estimate of the value of the activation energy by starting with the assumption that the observed rate of the polymorphic transition is the difference in rates of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ processes, i.e.,

$$V = a_1 e^{-E_1/RT} - a_2 e^{-E_2/RT}, \tag{1}$$

where E_1 and E_2 are the activation energies of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ processes, respectively, and T is the transition temperature. We shall assume the coefficients a_1 and a_2 to be independent of the temperature. Since $a \sim \exp(\Delta S/R)$, where ΔS is the entropy difference between the phases and the transition state, this amounts to assuming that the entropies of the phases and of the transition state show the same temperature-dependence. Equation (1) also assumes that the transition takes place at random throughout the boundary surface. We start with the assumption that the statistical unit is not an individual molecule but a mosaic block of the crystal. The mechanism of transition of the block (by dislocations, via two-dimensional nuclei, etc.) plays no role if the rate of transition within the block is much greater than the overall transition rate.

Since in the relation $T = T_0 \pm \delta$ we may assume that $\delta \ll T_0$, we can use the approximation

$$\frac{1}{1 \pm \delta/T_0} \approx 1 \mp \frac{\delta}{T_0},$$

so as to convert Eq. (1) into the form

$$V_{\alpha\to\beta} = a_1 \exp\left(-\frac{E_1}{RT_0} + \frac{E_1\delta}{RT_0^2}\right) - a_2 \exp\left(-\frac{E_2}{RT_0} + \frac{E_2\delta}{RT_0^2}\right), \quad T > T_0,$$

$$V_{\beta\to\alpha} = a_1 \exp\left(-\frac{E_1}{RT_0} - \frac{E_1\delta}{RT_0^2}\right) - a_2 \exp\left(-\frac{E_2}{RT_0} - \frac{E_2\delta}{RT_0^2}\right), \quad T < T_0.$$

From the condition that V = 0 when δ = 0, we have

$$V_{\alpha\to\beta} = A\left(e^{E_1\delta/RT_0^2} - e^{E_2\delta/RT_0^2}\right), \tag{2a}$$

$$V_{\beta\to\alpha} = A\left(e^{-E_1\delta/RT_0^2} - e^{-E_2\delta/RT_0^2}\right), \tag{2b}$$

where

$$A = a_1 e^{-E_1/RT_0} = a_2 e^{-E_2/RT_0}. \tag{3}$$

We shall compare with experiment the ratio of rates

$$\eta(\delta) = \frac{|V_{\alpha\to\beta}|}{|V_{\beta\to\alpha}|} = \exp\left(\frac{E_1 + E_2}{RT_0^2}\delta\right).$$

From the straight line

$$\ln \eta = \frac{E_1 + E_2}{RT_0^2}\delta \tag{4}$$

we can find the sum $E_1 + E_2$ of activation energies.

Curve (2a) has no maximum. Curve (2b) has a maximum, the condition for which (from $dV/d\delta = 0$) has the form

$$\frac{E_1}{E_2} = \exp\left(\frac{E_1 - E_2}{RT_0^2}\delta_{max}\right). \tag{5}$$

From Eqs. (4) and (5) we can find E_1 and E_2. In principle we can also determine the pre-exponential factors.

Using the experimental data shown in Figs. 6 and 7, we obtain: $E_1 + E_2 = 34.5 \pm 5$ kcal/mole, and $\delta_{max} = 12° \pm 2°$. We must add to this the obvious relation $E_1 > E_2$. The solution of the transcendental Eq. (5) gives the following final results:

$$E_1 = 17.4 \pm 2.5 \text{ kcal/mole}, \quad E_2 = 17.1 \pm 2.5 \text{ kcal/mole}.$$

These results permit us to assume that the heat of transition $Q = E_1 - E_2$ is no greater than ~1 kcal/mole.

Since we are considering a first-order phase transition, and such transitions are accompanied by a density discontinuity, we might expect that there are extended and compressed layers of molecules in the neighborhood of the boundary between the two media, and that these stresses extend on both sides of the boundary, gradually dying out. Might we assume that the large value of the activation energy is due to these elastic stresses? In the case of p-dichlorobenzene, the

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[1)] The transition-rate measurements were made on many crystals, and in general, on different (hk*l*) faces each time. However, steps were taken so that within any given crystal the V(n) measurements were made on the same growth faces, i.e., $(hkl)_\beta$ was the same for all odd n, just as $(hkl)_\alpha$ was for all even n.

density difference between the α- and β- phases is insignificant, being namely ~0.07%.[5] The energy of elastic compression or expansion by the corresponding percentage does not amount to even a hundredth of 17 kcal/mole. Consequently, we should seek an explanation for this high value in the deformation of the individual molecule in passing from one phase into the other.

In conclusion, we must note that the activation energies E_1 and E_2 obtained above are mean values. In fact, different growth faces have different activation energies, i.e., $E = E(hkl)$. Furthermore, if we wish to take into account the different growth mechanisms (by dislocations, by two-dimensional nuclei, involving the intermediate layer, etc.), we must introduce into the theory a spectrum of activation energies for each given (hkl). It is quite clear in this regard that the proposed system of calculation is highly provisional in nature.

3. Deviation from "ideal" experimental conditions. The experimental relation $V(\delta)$ shown here is not very precise. We can discern the following three fundamental sources of error:

A. The transition rate is a function of the defect content of the crystal, other conditions remaining equal. If we select for study sufficiently perfect crystals, and accept for calculation only those measurements in which the phase boundary moves smoothly, rather than by "jumps", this relation is not dominating, although it distorts the results perceptibly.

B. In our experiments, the indices of the growth faces of the new phase remained unknown. In going to another crystal, the indices of these faces were also changed, since they depended on the chance orientation of the nucleus giving rise to the "s-s" transition. By averaging the data over several crystals, we obtained a certain "mean" rate of polymorphic transition, which was the one used in the calculations. However, even it proves to be not very definite, owing to the insufficient statistics resulting from the great laboriousness of the experiment. There are grounds for assuming that the growth rates of the fundamental faces can differ among themselves by a factor of about three.

C. The inclination of the growth face to the surface of the crystal was also random. We did not take into account the inclination factor, although it can be taken into account, and this will be done in further experiments. According to estimates, the inclination factor increases the spread in the measured rates on the average by an additional factor of 1.5—2. However, it does not introduce a systematic error into the values of $E_1 + E_2$ and $\delta_{\max}$.

We can easily arrive at the conclusion that the causes pointed out above can give rise to a spread in the measured rates by a factor of as much as ~6, which is not in poor accord with the data of the table.

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Translated by M. V. King
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