

XCVIII.—*Studies in Polymorphism. Part I. A Preliminary Investigation of the Polymorphism of o-Nitroaniline.*

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WHILST studying the influence of various factors on the degree of supercooling of *o*-nitroaniline, one of us (J. F. J. D.) noticed that on certain occasions, notably when supercooling was large or the rate of cooling rapid, the solid was much lighter in colour than was normally the case. Suspecting polymorphism, we examined the behaviour of the substance during its crystallisation in a thin film between a microscope slide and a cover-slip, and found that it does, in fact, crystallise in two forms. Under ordinary conditions solidification starts from a number of nuclei and proceeds from them radially in the form of closely packed needles. Viewed by transmitted light, some of the resulting spherulites are seen to be composed of dark orange crystals, and the remainder of yellowish-green crystals. These two forms have been examined crystallographically under the microscope by Mr. Alan Stuart, of the Geology Department of this College, who reports as follows: "The dark orange crystals—length direction is the direction of fast vibration, pleochroic, straight extinction, biaxial, therefore orthorhombic. The yellowish-green crystals—length direction is the direction of fast vibration, slightly pleochroic, oblique extinction of about  $24^\circ$ , therefore monoclinic or triclinic."

Difficulty was at first experienced in obtaining crystals sufficiently large for this microscopic examination, especially in the case of the green form, which normally appears in extremely fine needles. This difficulty was eventually surmounted by remelting the centre portion only of a freshly crystallised melt on a slide by means of a little circular hot plate. This gave a liquid surrounded by crystals of both forms, and on cooling, each inoculated its own species from the melt. Supercooling was thus prevented and the slow growth which took place just below the melting point resulted in comparatively large crystals.

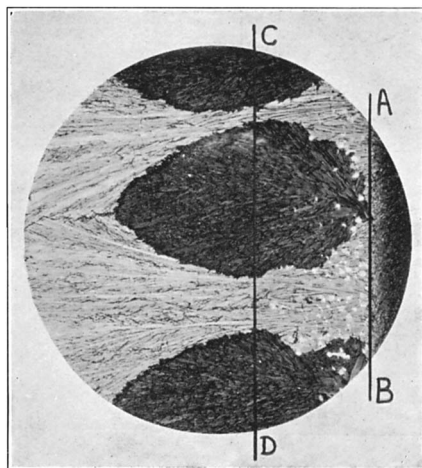
The crystal structure of *o*-nitroaniline has been studied by the X-ray method by Hermann and Burak (*Z. Krist.*, 1928, **67**, 189), who concluded that it was orthorhombic. The only mention of its polymorphism appears to be a statement by Kohman, in a study of the freezing points of binary mixtures of the nitroanilines (*J. Physical Chem.*, 1925, **29**, 1048), to the effect that the substance in binary mixture gave indications of existing in an unstable form.

We therefore decided to study the phenomenon in more detail, especially as the regular appearance of the two modifications side by side appeared to facilitate the investigation of certain aspects of polymorphism, such as the rate of stabilisation.

In about two hours after solidification the orange crystals are seen to have commenced to extend their territory at the expense of the green variety, showing that the former is the more stable modification. In addition, isolated crystal grains of the orange form appear in the areas occupied by the green form and continue to grow. This transformation occurs at all temperatures between that of the room and the melting point ( $70^{\circ}$ ), becoming much more rapid as the latter is approached, so within this range the polymorphism is monotropic.

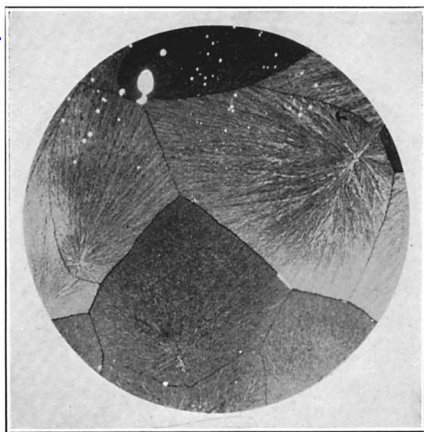
The reason for the simultaneous appearance of the two forms under ordinary conditions of cooling, *i.e.*, radiation to room temperature, is that, within the temperature range in which crystallisation starts, the number of nuclei of each formed and their crystallisation velocities are of the same order, although there is usually a preponderance of the unstable form. More nearly equal quantities are produced if the slides are allowed to radiate to an atmosphere at about  $30^{\circ}$ ; and at still higher temperatures of the environment, the proportion of the stable form is increased until, just below the melting point, no unstable form at all is obtained. The main factor determining this behaviour appears to be the relationship between the crystallisation velocities of the two forms at different temperatures, which is well illustrated by Fig. 1. This photomicrograph depicts the crystallisation on a slide of some nitroaniline that had been melted except for the strip of solid to the right of the line AB, which contained both forms. On cooling, the stable (dark) form at first grew the more rapidly, as is shown by the constriction of the unstable areas; then both forms crystallised at the same speed (CD), and after this stage the stable form separated less rapidly, finally becoming entirely suppressed.

The numbers of nuclei of the two forms, however, appear to go more nearly hand in hand with alteration in the temperature, both increasing considerably as the temperature is lowered. On a slide, a melt which is rapidly cooled or greatly supercooled, appears to the naked eye to crystallise rapidly from a large number of nuclei of the unstable form. Microscopic examination, however, shows that there are numerous crystals of the stable form embedded in the mass, which evidently have not had a chance to grow owing to their small crystallisation velocity at the temperature of their formation. These small stable crystals are also seen under the microscope in the unstable areas of melts which have crystallised more slowly (see

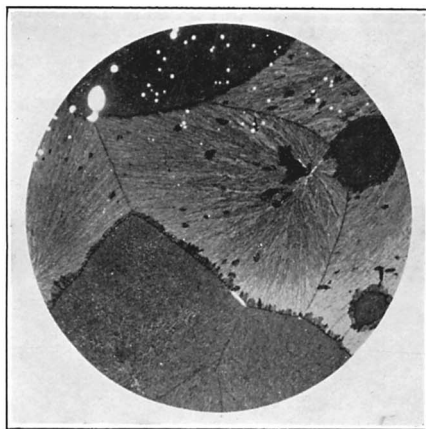


*Direction of falling temperature and crystallisation ( $\times 20$ ).*

FIG. 1.



*Soon after crystallisation.*

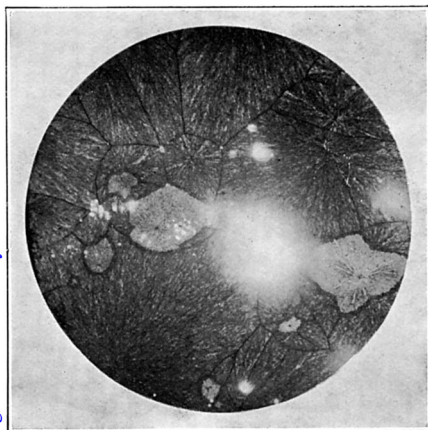


*21 Hours later.*

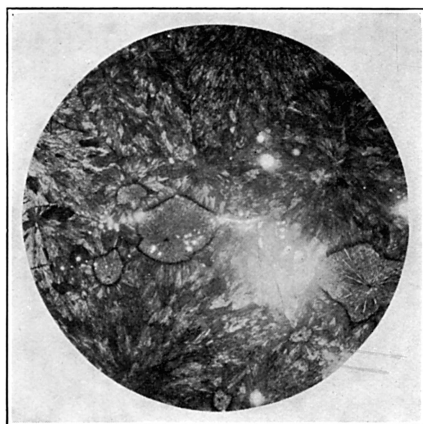
*"Crude" o-nitroaniline (the dark material is the stable form) ( $\times 5$ ).*

FIG. 2.

[To face p. 726.]



*Soon after crystallisation.*

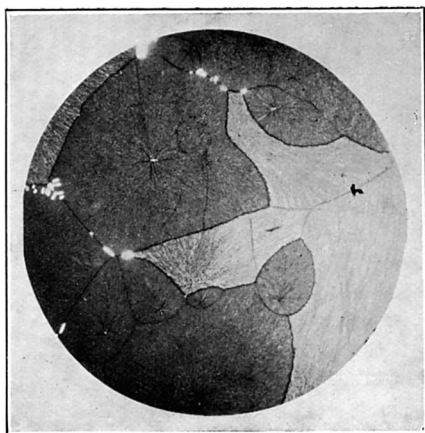


*21 Hours later.*

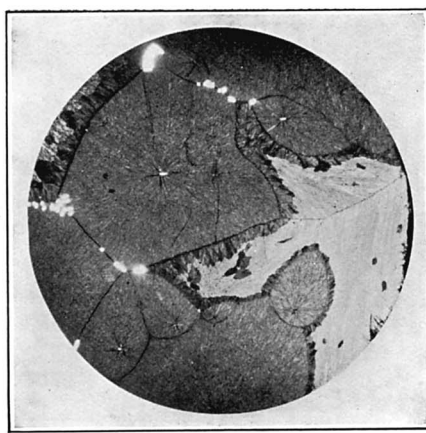
*o-Nitroaniline twice recrystallised from alcohol ( $\times 5$ ).*

*(The stable form here appears lighter than the unstable form owing probably to the film being thicker than in Figs. 2 and 4.)*

FIG. 3.



*Soon after crystallisation.*



*21 Hours later.*

*o-Nitroaniline (twice recrystallised from alcohol) + 0.9% of p-nitroaniline ( $\times 5$ ).*

*(The dark material is the stable form.)*

FIG. 4.

next section). They apparently give rise to the previously mentioned, isolated crystal grains visible to the naked eye after stabilisation has proceeded for some time.

*The Rate of Stabilisation.*—In the thin films studied the time taken for the transformation of all the substance into the stable form depends on two factors: (1) the linear stabilisation velocity, *i.e.*, the rate at which the boundary between the stable and the unstable form moves in a direction normal to itself, and (2) the length of the boundary. In any given specimen it may be assumed that (1) remains constant at constant temperature (provided that any impurity present is evenly distributed throughout the film), if the boundary be so long and the crystals so small that the observed effect is a statistical average of the velocities at different crystal faces. Factor (2) will depend mainly on the proportion of the stable form present as small grains, for if this is large, not only will the total length of boundary be very great at the start, but it will increase rapidly as stabilisation proceeds. We have found that both these factors are greatly affected by small variations in the degree of purity of the substance (compare Tammann, "The States of Aggregation," English transl., Constable and Co., 1926, pp. 228 *et seq.*).

The starting point of all these experiments was Schuchardt's "pure" preparation, stated possibly to contain a trace of *p*-nitro-aniline, and hence subsequently referred to as "crude." On slides made from this material and kept at room temperature, stabilisation was very slight after 21 hours (see photomicrographs, Fig. 2) and was not complete until several days had elapsed. A quantity of the crude substance was recrystallised five times from absolute alcohol, a specimen of each stage being retained and dried in the ordinary way. After about one week's storage in a calcium chloride vacuum desiccator they had lost all odour of alcohol. On slides made from these specimens, stabilisation was much more rapid than on those made from the crude substance (Fig. 3; contrast Fig. 2), and was usually complete in 24 hours, this being due to a considerable increase in both the linear stabilisation velocity and the number of small grains. From this result it appeared either (1) that the crude material contained an impurity acting as a retarding agent, or (2) that the recrystallised substance retained traces of alcohol which acted as an accelerator. The second possibility did not appear to be very probable, for the manufacturers had informed us that their product was also recrystallised from alcohol, and it was not likely to have been more completely dried than ours. However, after our specimens had been kept for 12 months in a calcium chloride desiccator, they became distinctly slower, but this appeared



to be due to a diminution in the number of small grains rather than to any alteration in the linear stabilisation velocity.

In order to test the first possibility, mixtures of some of the recrystallised specimens with about 1% of *p*-nitroaniline were made, since this was one of the most likely impurities. According to the results of Kohman (*loc. cit.*), this proportion of the *p*-isomeride lowers the f. p. of *o*-nitroaniline by about 0.6°, which is the average difference found between the purest recrystallised specimens and the crude material (see Table I, p. 731). These mixtures were intermediate between the crude and recrystallised specimens as regards both the linear stabilisation velocity and the number of small grains formed (compare Figs. 4, 3, and 2). The slowness of the crude substance is therefore not due to *p*-nitroaniline alone, although this substance may be partly responsible.

Two other methods of purification were tried, *viz.*, steam-distillation and distillation directly on to a microscope slide. The yield in the first case was small, and the product behaved as regards stabilisation in much the same way as the recrystallised specimens before prolonged drying, but was possibly a little slower. In the second case, one of the recrystallised specimens was placed in a short Pyrex test-tube held in a vertical position by being surrounded with sand contained in a large iron crucible. The latter was heated and the substance fractionally sublimed on to a series of microscope slides laid in succession on the top of the test tube. The first and middle fractions stabilised as rapidly as the recrystallised specimens, but the last fractions were exceedingly slow, the last of all being much slower even than the crude substance, only a very small amount of stabilisation having taken place after 4 days. Under the microscope these slow specimens were seen to be contaminated with a liquid, evidently a decomposition or oxidation product, for the residue in the test tube was charred. This liquid appeared to be much less volatile than the nitroaniline, for, whereas on long keeping, the latter always evaporates considerably at the edges of the cover slip, this liquid did not do so. The slowness of these specimens is evidently connected with this impurity.

In these and all other experiments described in this paper, the slides and cover-slips were treated with hot chromic or chromic-nitric acid mixture, it being ensured by the use of suitable holders that the liquid had free access to all surfaces. They were then washed with distilled water, next with conductivity water, and were finally dried in an air-oven and stored in a calcium chloride desiccator. In the later experiments, they were also steamed for a few minutes before being dried. To prevent decomposition of the substance, the hot plate used for melting the films was fitted with a thermometer

and the temperature was never allowed to rise above  $120^{\circ}$ , nor were the slides left on the plate longer than was absolutely necessary. In preparing the slides, they and the cover-slips were manipulated entirely with forceps. The progress of stabilisation was conveniently followed by projecting the slides at intervals on to a screen by means of an optical lantern.

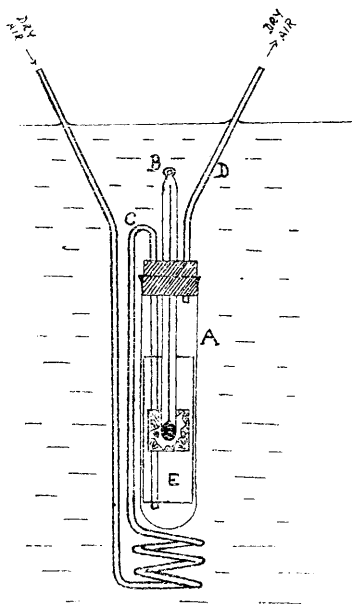
After the stabilisation process described above is complete, most slides on standing for some weeks develop dark brown patches which gradually extend. This change, which is being further studied, is partly due to the coalescence of the original needles to form larger crystals.

*Freezing Points and Melting Points.*—In order to compare the purity of the different specimens obtained by recrystallisation, an attempt was made to determine their freezing points. This proved to be impossible with the quantities available (about 2 g. of each), for the freezing point registered depended entirely on the bath temperature even when the latter was only  $1^{\circ}$  or  $2^{\circ}$  below the former. This is probably because the substance has a low velocity, or heat of crystallisation, or both. The highest temperature registered by the crude substance was  $68.7^{\circ}$  with the bath at  $67^{\circ}$ , and  $68.9^{\circ}$  with the bath at  $68^{\circ}$ . The thrice recrystallised specimen had a f. p. of  $69.2^{\circ}$  with a bath temperature of  $68^{\circ}$ , and this was the highest temperature observed. (Determinations with the fourth and fifth fractions, however, were not made.) This value may be compared with Kohman's, *viz.*,  $69.3^{\circ}$  (*loc. cit.*).

Attention was next directed to melting-point determinations. The m. p.'s given in the literature vary from  $68^{\circ}$  to  $71.5^{\circ}$ . The ordinary methods proved quite unsatisfactory, since it seemed impossible to judge with certainty to less than  $0.5^{\circ}$  the temperature at which melting began, even when the melting-point tube was observed with a low-power microscope. In order to remove any unstable form, the tubes were heated at  $60^{\circ}$  for some days, but this did not seem to make any difference. The difficulty was eventually overcome by means of the apparatus shown in Fig. 5, in which the melting of the substance on microscope slides could be observed. This method had the advantage that the melting points of both forms could be determined in one operation. The glass tube, A, which was just wide enough to contain a  $3'' \times 1''$  microscope slide, E, was fitted at the top with a rubber stopper carrying an Anschütz thermometer of the enclosed-scale type, B, graduated from  $60^{\circ}$  to  $85^{\circ}$  in  $0.2^{\circ}$  (made specially for this work by Messrs. Negretti and Zambra), and two  $\frac{1}{8}''$  copper tubes, C and D. The tube C, which was about one yard long, passed to the bottom of A, being coiled outside as shown. The tube D reached just below the

stopper. The slide was supported between the tube C and the thermometer, the bulb of the latter being opposite the centre of the substance under the cover-slip. The whole apparatus was immersed to the level shown in a 2-litre beaker containing water and fitted with a mechanical stirrer, a thermometer, and a movable 2-volt electric bulb enclosed in a frosted glass tube, by means of which any desired portion of the material on the slide could be brightly illuminated from behind. The beaker was heated by a shielded gas flame controlled by a fine adjustment. By attaching D to a filter pump

FIG. 5.



and C to a sulphuric acid wash bottle a rapid current of dry air at the same temperature as the outer bath could be drawn through A. Careful trials showed that, provided the temperature of the bath was not altered more rapidly than  $1^{\circ}$  in 10 minutes and a rapid current of air was drawn through A, the temperature registered by the thermometer kept the same, to within  $0.1^{\circ}$ , as that of the bath. Since the substance on the slide was only separated from the air stream by the thin cover-slip, it did not seem possible for it to lag behind the thermometer in acquiring the temperature of the air, especially as the slide and thermometer had approximately equal volumes and therefore approximately equal heat capacities. (As is well known, glass has very nearly

the same heat capacity as an equal volume of mercury.) If proof were needed, however, it was furnished by the fact that if the temperature of the apparatus were rapidly raised so that there was considerable lag on the part of the thermometer, then the substance on the slide melted at a very much lower reading than when slow heating was used. Thus, under conditions such that the thermometer registered the temperature of the bath, it also registered the temperature of the *o*-nitroaniline. These conditions, already specified, were adhered to during the melting-point determinations.

In carrying out a determination, a freshly crystallised slide containing both the stable and the unstable form was placed in A, and the apparatus rigidly fixed in the bath which had been previously



heated to 65—67°. If this preliminary heating were omitted, it was found that the long time taken to raise the apparatus to the m. p. resulted in complete stabilisation of the substance, so that the m. p. of the unstable form could not be observed. The air stream was then started, and the bath rapidly stirred. When the inner and outer parts were in thermal equilibrium the temperature was allowed to rise at the above-mentioned rate. A suitable portion of the slide, usually near the bulb of the thermometer, was illuminated and observed by means of a low-power microscope. The unstable areas melted first and left crystals of the stable form surrounded by liquid. One or two well-shaped crystals were selected for observation and watched carefully against an eye-piece scale in the microscope. The temperature at which they first showed signs of melting could thus be determined very sharply. The point at which the unstable form commenced to melt could not be determined so precisely, for this form usually consisted of very small crystals packed closely together, and consequently there were no sharply defined crystal edges visible. Moreover, melting at the boundaries between the stable and the unstable form was often observed to take place at a lower temperature than that at which the bulk of the unstable form melted.\* The temperature recorded as the m. p. was that at which melting some distance from the boundary first became apparent.

Objection may be raised to this method on the ground that substances in thin films have lower melting points than when in bulk; for example, Meissner (*Z. anorg. Chem.*, 1920, **110**, 169) has shown that the m. p. of a film of myristic acid decreases by 0.3° as the thickness diminishes from 10  $\mu$  to 0.8  $\mu$ . Measurements of the thickness of four of our films taken at random gave the values 0.135, 0.155, 0.145, and 0.125 mm., which would appear to be well outside the range of this effect.

The results are given in Table I. With the exception of the crude specimen they refer to material dried for 12 months over calcium chloride.

TABLE I.

Specimen.	Crude.	Fractions of recrystallised specimens.					
		1.	2.	3.	4.	5a.†	5b.†
M. p. of unstable form.	ca. 67.9°	ca. 68.1°	68.1°	68.1°	68.3°	ca. 68.2°	68.2°
M. p. of stable form.	69.5	70.05	69.9	70.1	70.15	70.15	70.1
	69.5	69.9		70.1	70.15	70.25	

† Results with two different slides.

\* This may be a surface effect, or may be due to a concentration of traces of impurity at these places. It is also not impossible that, owing to differing molecular complexity, the two forms melt to give for a brief period different liquids, so that the m. p. of one is lowered by contact with the other.

The values for the 3rd, 4th, and 5th fractions show little difference, so that probably the maximum purity possible by the method of purification used was reached. From the average of these three specimens, the m. p. of the unstable form lies  $1.9^{\circ}$  below that of the stable form. The values must, of course, be higher than the true solid-liquid equilibrium temperature. Kohman's value of  $69.3^{\circ}$  seems, however, to be too low, for on one occasion it was noted that when a slide was cooled the crystals started to grow above  $69.5^{\circ}$ . Possibly his determination was influenced by the same factors as were our freezing-point determinations, for he too used a small quantity. It is also possible that his specimen was impure, for he states that sublimation was used as one of the methods of purification and as already stated this may lead to decomposition or oxidation.

*Summary.*

1. *o*-Nitroaniline exists in two polymorphs. One (m. p.  $68.1$ — $68.3^{\circ}$ , monoclinic or triclinic) is unstable at all temperatures between that of the room and the m. p. and changes into a stable form (m. p.  $70.1$ — $70.2^{\circ}$ , orthorhombic).

2. When the substance is crystallised in thin films, both forms are normally obtained, the relative amounts depending on the temperature at which crystallisation begins. This has been connected with the relation between the crystallisation velocities of the two forms at different temperatures.

3. The time taken for the disappearance of the unstable form has been studied with regard to (i) the linear stabilisation velocity at the stable-unstable boundary and (ii) the extent of the boundary; and the effect of impurities on both these factors has also been investigated.

4. An apparatus which enables the melting points of both forms to be determined in the same operation is described.

In conclusion, we wish to express our gratitude to Mr. Alan Stuart for his interest and assistance in the crystallographic part of this work.

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[Received, February 8th, 1930.]