Kinetics of a Polymorphic Transformation of Azoxybenzene.

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A new monotropic polymorph of azoxybenzene has been characterised, and the kinetics of its transformation into the stable form under thin-film conditions have been investigated over the range 0—30°, a photometric method being used for the measurement of transformation rates. With highly purified material, the transformation is strictly linear with time, independent of film thickness, and relatively free from difficulties caused by spontaneous nucleation. The results agree well with the mechanism proposed by Hartshorne for polymorphic transformations, the energy of activation being 22·5 ± 1 kcal./mole (the heat of transition being assumed as 1 kcal./mole), and the temperature-independent factor very large. The activation energy agrees closely with 23 ± 1 kcal./mole, the heat of sublimation of the metastable form. The latter has been determined by an effusion method, the heat of transition being assumed to be as above. An approximate doubling of the rate after exposure to ultra-violet light is reported and discussed. The transformation is shown to parallel that of monoclinic ⟶ rhombic sulphur in several respects.

Little is known of the mechanism of polymorphic transformations and few kinetic measurements of this type have been reported. The scarcity of data is due mainly to the difficulty of finding examples which undergo transformation in an easily measurable fashion. Experience with a polymorph of azoxybenzene (Campbell, Henderson, and Taylor, *Mikrochem. Mikrochim. Acta*, 1951, **38**, 376) suggested that this might be a suitable case for study, and further work has revealed a second monotropic polymorph which is transformed into the stable modification in a manner eminently suitable for kinetic measurements. The results here presented lead to the same mechanism as that proposed by Hartshorne and his co-workers (*Discuss. Faraday Soc.*, 1949, **5**, 149; *J.*, 1951, 1097) for the monoclinic ⟶ rhombic sulphur transformation, *viz.*, one based on the difference in rates of escape of molecules from the two adjacent lattices, and requiring the full latent heat of sublimation of the metastable form as energy of activation.

Experimental and Results.

Preparation and Purification.—Azoxybenzene was prepared by sodium methoxide reduction of pure nitrobenzene and purified by crystallisation from aqueous methanol, followed by chromatography on a benzene–alumina column and a further crystallisation. These operations were carried out under red light owing to the ease with which the pale yellow azoxybenzene developed an orange colour when exposed to white light in contact with solvents (cf. Badger and Buttery, *J.*, 1954, 2243). Final purification was by distillation at a pressure $<10^{-5}$ mm. in a vertical tube (10″ × 1½″), also under dark-room conditions. The impure material in the bottom of the tube was kept molten by means of a water-thermostat at 50°, the lowest temperature at which a reasonable rate of distillation occurred, while the upper half of the tube was cooled to 10°. The condensate obtained during the first 12 hr. had a slight orange tint and melted over the range 35—36·2°. This material was completely removed from the tube, and the second fraction collected during the next 24 hr.; it was very pale yellow, and its melting range was 35·6—36·4°. A third fraction, collected in the same manner, was again very pale yellow, but was contaminated with an unknown impurity which extended the melting range to 32—35·5°. All melting data were obtained at very slow rates of heating, a hot-stage microscope with high magnification and a calibrated thermometer being used. Without these stringent conditions, the difference between the first two fractions (apart from colour) would have been barely detectable, and indeed, under the same conditions several " AnalaR " standard substances rarely showed melting ranges of less than 0·5—1·0°. The second fraction was therefore considered to be very pure and was used in all kinetic and vapour pressure measurements.

Characterisation of the Polymorphs.—The polymorph described by Campbell, Henderson, and Taylor (*loc. cit.*) was readily obtained by cooling to 0° a liquid film of azoxybenzene held between a microscope slide and cover slip. It appeared as well-formed spherulites with brilliant polarisation colours and melted at 29°. This form is now designated III, the stable form being I. The transformation III → I occurred at a convenient rate at room temperature, but quantitative measurements with a travelling microscope were eventually abandoned, owing partly to a high degree of spontaneous nucleation, but mainly to the discovery of a further polymorph, designated II, whose transformation to I under thin-film conditions proved much more satisfactory. At a film thickness of 0·02 mm., form II showed a pale brownish-yellow colour under crossed Nicols, in contrast to the brilliantly coloured spherulites of III and the slightly less coloured needles of the stable form I. The final m. p. of II was 36·2°, only 0·2° less than that of the stable form. The transformation II → I was characterised by a slower rate than the III → I process, very little spontaneous nucleation, and a well-developed interface between the two forms. Furthermore, during the II → I transformation, the film became more opaque, and this fact was utilised in developing a photometric method for measuring the rate of the transformation (see below). No reversible transition points were observed and the relationship between the forms in all cases is therefore monotropic.

In view of the slight difference (0·2°) between the m. p.s of forms I and II, further characterisation of II was sought by means of X-ray powder photographs, using a Unicam 9-cm. camera with copper K_α radiation. Normally, the powdering of II would have resulted in its transformation to I before a satisfactory photograph could have been obtained. However, with the third fraction of azoxybenzene obtained in the vacuum-distillation, the transformation II → I was found to be almost completely inhibited, probably owing to some slight impurity, and a powder photograph of II could therefore be obtained. Photographs of I from fractions two and three were identical, while that of II was distinctly different from that of I. Spacings in Å are as follows:

Form I ...	9·01m	5·77w	5·36m	4·65s	3·86s	3·55m	3·22w	3·03m	2·70w	2·29w
Form II ...	8·41m	5·60w	4·58s	4·26s	3·78s	3·17w	3·05m			

(s = strong; m = medium; w = weak)

Density Determinations.—The densities of I and II (fraction three again being used), determined at 20° by flotation in water–sulphuric acid mixtures, were found to be 1·260 and 1·251, respectively.

Establishment of the Linearity with Time of the II → I *Transformation.*—In view of the higher density of form I, a small contraction away from the II—I interface may occur during the transformation, leading to a fall in rate with time (cf. Hartshorne *et al.*, *J.*, 1935, 1860; *J.*, 1938, 1636). A method of ascertaining whether or not the transformation remained linear with time was therefore necessary. A film of form II, 25 × 37 mm. and 0·025 mm. thick, was prepared between two microscope slides and seeded along one long edge with form I by scratching with a sharp point and painting with a slurry of form I in ethanol. Experiment showed that the use of this slurry had no effect on the transformation other than ensuring complete nucleation along the whole front. The film was kept at constant room temperature in diffused artificial light and photographed at 15-min. intervals, after which the negatives were projected with approximately 15-fold enlargement on to graph paper, and the successive II—I interfaces traced. The areas of transformation obtained in equal intervals of time for a fixed width of interface were cut out with a razor blade and weighed. Since the graph paper was of uniform weight per unit area, a relative measure of the rate of transformation was obtained from the weights of paper cut out. For two films, the transformation was found to be strictly linear with time.

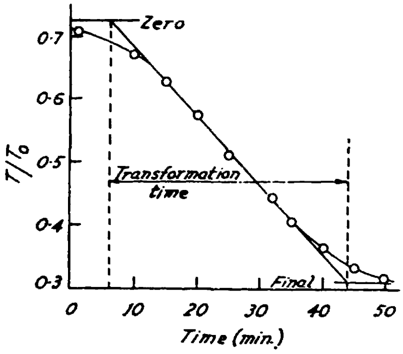
Effect of Film Thickness.—A film was prepared as above with the addition that at one end the microscope slides were held apart with a piece of copper foil, thus producing a wedge shaped film varying from 0·002 to 0·095 mm. in thickness at right angles to the direction of growth, but of uniform thickness along any line parallel to the direction of growth. The transformation was photographed and traced on uniform graph paper as before. This tracing was then divided into three sections of equal width across the direction of growth, each section representing a different average film thickness, and the areas of transformation were cut out and weighed. All three sections showed the same constant rate of transformation. Furthermore, no correlation was ever found between film thickness and transformation rate as measured by the Spekker method described below.

Spekker Absorptiometer Method for measuring Transformation Rates.—Consider a rectangular film of azoxybenzene form II of uniform thickness and area a supported between glass slides. If the film is completely immersed in and at right angles to a uniform light beam of intensity I_0 per unit cross-section area and of total area a_0 ($a_0 > a$), then the total amount of transmitted light is

$$T = I_0(a_0 - a) + I_2a - K$$

where I_2 is the intensity of the beam transmitted through unit area of the film, and the constant K allows for the light absorbed and scattered by the glass support. This equation may be simplified to $T = \text{const.} - a(I_0 - I_2)$. Let this film now be seeded along one edge with form I, and after times t' and t'' let areas a' and a'' respectively have been transformed to the stable modification. Let I_1 be the intensity of the light transmitted by unit area of form I, and the total light transmitted at t' and t'' be T' and T'', respectively. Then

FIG. 1.



$$T' = \text{const.} - a'(I_0 - I_1) - (a - a')(I_0 - I_2)$$

and

$$T'' = \text{const.} - a''(I_0 - I_1) - (a - a'')(I_0 - I_2)$$

The rate of change of total light transmitted is

$$(T'' - T')/(t'' - t') = (a'' - a')(I_1 - I_2)/(t'' - t')$$

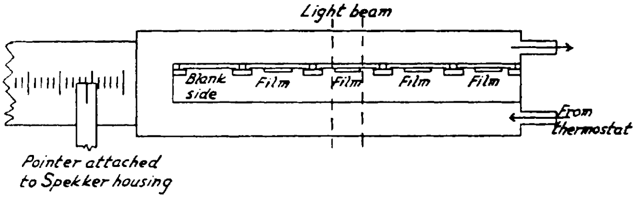
and is therefore a measure of the rate of change of area transformed. The latter, it should be noted, is a measure of the linear rate of advance of the interface only if the film is of uniform width perpendicular to the direction of growth, and provided no further nucleation occurs. Oblique growth of form I from " dark " regions of the film into the light beam would constitute further nucleation from the point of view of the theory. This was eliminated by having the film completely bathed in the beam in a lateral direction, and by the fact that spontaneous nucleation either along the edges or within the body of the film rarely occurred.

In using the Spekker instrument for rate measurements, it was balanced in the normal way with the solution position occupied by the transforming film, and the solvent position by a microscope slide. Thus at times t' and t'', values of T'/T_0 and T''/T_0 respectively were obtained by inverting the antilog of the drum reading, T_0 being the light transmitted by the blank slide. The rate of change of T/T_0 is $(a'' - a')(I_1 - I_2)/\{(t'' - t')T_0\}$ and is therefore directly proportional to the rate of transformation. Since the latter is constant at a given temperature, the plot of T/T_0 against time is a straight line, the gradient being proportional to the rate. A difficulty arises, however, if all the films do not have the same thickness, for this leads to variation in I_1 and I_2, and the rate of change of light transmitted would vary from film to film even although the actual rate of transformation was the same for each. Furthermore, owing to irregularities in the advancing front, the whole of the front does not enter or leave the beam simultaneously and causes the T/T_0–time graph to be curved at the beginning and end of the measurements. These troubles were eliminated by extrapolating the central linear portion of the graph to the zero and final values of T/T_0 (see Fig. 1). The latter can easily be measured if the direction of growth is vertical and the film extends a few mm. above and below the vertical limits of the beam. From the extrapolation, the time required for that part of the film totally immersed in the light beam to be transformed completely is obtained.

A further requirement is that the light beam should be of uniform intensity along the direction of growth, otherwise a linear rate of transformation would not result in a linear change in the amount of light transmitted. Since photographs showed the Spekker beam to be of uniform intensity along its vertical axis in the slide position, experiments were always carried out so that the front advanced from the bottom to the top of the beam.

Preparation of Films and Measurement of Rates of Transformation.—Films of form II were prepared between microscope slides and cover slides 25 mm. long by 11 mm. wide, the corresponding light beam dimensions being 14 × 12 mm. The measured transformation times therefore corresponded to a 14-mm. advance of interface and a transformed area of 14 × 11 mm.^{2}. Under red-light conditions, a small quantity of powdered azoxybenzene was melted between a slide and cover slip at 40° on an electrically heated aluminium block, care being taken to exclude air bubbles. The slide was then cooled for 5 min. on a plane horizontal brass surface kept by thermostat at 20°, after which the film of supercooled liquid was seeded along its lower 11 mm. edge with form II. Complete crystallisation occurred in less than 2 sec.

FIG. 2.



By using the same volume of powder (as judged by eye), films were readily obtained, with practice, having uniform thickness within the range 0·02—0·1 mm., for which, as shown above, the rate is independent of thickness. Since prolonged heating at 40° caused some increase in rate, the heating was limited to 1·5 min. for a first melt and 0·5 min. for a second. Only first and second melts were used in the quantitative work, even although no detectable increase in rate occurred after three melts. The same lower edge was now scratched with a sharp point and painted with a slurry of form I in ethanol. Occasionally, transformation of the slight crust along the vertical sides of the film was more rapid than transformation within the body of the film, causing side nucleation and therefore non-linear plots of T/T_0 against time. This tendency was minimised by terminating the scratch 1 mm. from each end of the edge. This procedure for preparing films had to be rigidly adhered to, otherwise considerable variation in rate occurred. Even so, rates varied appreciably from one preparation to another, and accordingly a single middle fraction was used in all measurements.

The films were now transferred to the inner compartment of the double Perspex box shown in plan in Fig. 2. This box was mounted on a brass slide of the same cross-section as that which normally carried the cell-holder, and thus with the aid of the pointer and scale any one of the four films or the blank slide could be positioned accurately in the light beam. Experiments were carried out at 5° intervals between 0° and 30°, water or an ethylene glycol–water mixture being used as thermostat fluid. For measurements at or below 10°, the Spekker instrument was totally enclosed within a dry box provided with suitable windows and port-holes. Measurements below 0° were impossible owing to cracking of the films, and above 30° owing to nucleation difficulties. Red filters (Hilger No. 603) were used on the Spekker absorptiometer so that no wave-length shorter than 6000 Å reached the films.

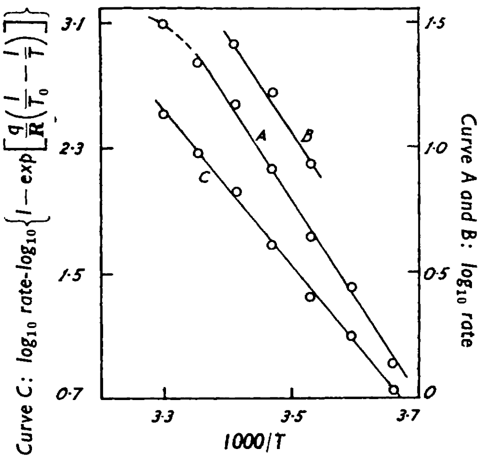
Results for Measurements in Red Light.—The results for a typical exeriment at 25° are given in Fig. 1 and show that the requirements of the theory given above were adequately fulfilled. In the Table are given the arithmetic mean rates, expressed as $10^3 \times$ (transformation time in min.)$^{-1}$, together with the number of experiments on which the mean is based, the standard deviation, and the coefficient of variation. The graph of $\log_{10}$ (Rate) against the $1/T$ is given in Fig. 3, line *A*. By statistical calculation using regression equations (Weatherburn, "First Course in Mathematical Statistics," Cambridge Univ. Press, 1945) and omitting the 30° point, the equation for *A* was shown to be $\log_{10}$ (Rate) $= -3932/T + 14{\cdot}55$, from which an apparent

Rates of transformation.

Temp.	0°	5°	10°	15°	20°	25°	30°
			Red light conditions				
Rate	1·390	2·778	4·422	8·180	14·80	21·89	31·33
No. of expts.	16	14	12	19	28	27	22
Standard deviation (*S*)	0·124	0·181	0·358	0·532	2·74	5·10	3·57
Coeff. of variation (*S*/Rate)	0·089	0·065	0·081	0·065	0·185	0·233	0·114
			After pre-irradiation with ultra-violet light.				
Rate	—	—	8·49	16·44	25·55	—	—
No. of expts.	—	—	12	18	15	—	—
Standard deviation (*S*)	—	—	0·855	1·67	3·44	—	—
Coeff. of variation (*S*/Rate)	—	—	0·101	0·102	0·135	—	—

activation energy of 17·9 kcal. (standard deviation 0·45) was obtained on the assumption (see p. 496) that the rate of the transformation can be represented by an Arrhenius-type equation. The 30° point was omitted from the calculation because it was shown to lie more than three standard deviations below the calculated line through the other six points, thus indicating a slight curvature at the high-temperature end of *A*.

Fig. 3.



Influence of Pre-irradiation with Ultra-violet Light on Rate of Transformation.—Variations in rate up to 100% in the early stages of the work were found to be due to exposure of the films (prepared under otherwise standard conditions) to bright daylight. Semi-quantitative experiments at 20° showed that irradiation of form II films with a Hanovia ultra-violet lamp at a distance of 30 cm. before seeding with form I, followed by transformation in red light, gave increased rates up to *ca.* 100% after 5 minutes' irradiation, with no further increase up to 10 minutes' irradiation. On re-melting and re-transformation of the films without further irradiation, the rates tended to return to normal red-light values. This tendency was greater the shorter the period of irradiation. If the irradiation was carried out with the films in the liquid state (*i.e.*, before being seeded with form II), 10 seconds' exposure was sufficient to cause the maximum increase in rate (again *ca.* 100%). In this case the effect was more permanent, several re-melts and re-transformations being necessary before any noticeable decrease in rate occurred. Quantitative measurements were carried out at 10°, 15°, and 20°, the films being prepared in the same manner as for the red-light work, with the addition of 15 seconds' irradiation before seeding with the metastable form. Experiments below 10° were impossible owing to cracking of the films on cooling, and above 20° owing to difficulty of securing complete nucleation with form I at all points simultaneously along the lower edge of the films. Results are given in the Table and plotted in Fig. 3, line *B*. In view of the small number of points, little confidence can be attached to the slope of line *B*, but the indication is that no change in apparent activation energy occurs after irradiation.

Temperature Rise at the II–I *Interface during Transformation.*—Calculated by Hartshorne and Roberts's procedure (*J.*, 1951, 1097), the temperature rise at the interface was found to be of the order 0·03°, reasonable values for the specific heat and thermal conductivity of azoxybenzene being assumed by comparison with other organic compounds. This rise is very little more than the variation in the temperature of the thermostated Perspex box, and would have no significant effect on the rate measurements.

Vapour-pressure Measurements and Heat of Sublimation of Form I.—Vapour pressures were determined by Knudsen's effusion method (*Ann. Physik*, 1909, **29**, 179), a cylindrical brass effusion cell closed with a platinum foil diaphragm soldered to a screw-on lid being used. The construction was such that the azoxybenzene was contained within a perfect cylindrical volume 9·52 mm. long and of 4·76 mm. radius, the axially placed orifice in the 0·014-mm. thick platinum foil being 0·905 mm. in radius. During effusion in a vacuum better than 5×10^{-6} mm., the cell was contained in a vertical copper tube, 3″ long by 1″ in diameter, fused at the upper end to a B34 Pyrex joint and closed at the lower end by a copper disc brazed on to the tube. The lower end of the tube contained a Wood's metal plug fused to the copper and having a cylindrical recess which was a close fit to the effusion cell. The latter was thus in good thermal contact with the water thermostat surrounding the copper tube, the top of which was 2″ below the surface of the water. The minimum distance between the cell and the cold surface of a liquid-oxygen trap connected to the Pyrex joint was 8″. The same material (well ground) being used as for the kinetic measurements, effusion was carried out at the desired temperature for several hours before the first weighing of the cell. Thereafter, five successive weighings were carried out after effusion for intervals of 400—3000 min. depending upon the vapour pressure, the loss in weight in any intervals being 10—30 mg. After the pumps had been switched on, 5 min. elapsed before the commencement of the timing of any interval to allow the pressure to fall to $<10^{-3}$ mm. Calculated in the usual manner, the five values of the vapour pressure at any one temperature did not differ by more than a few units % from the arithmetic mean value. By Whitman's method (*J. Chem. Phys.*, 1952, **20**, 161), the above cell dimension being used, the probability factor W for the cell was found to be 0·959. Theoretically this value of W is applicable only when the cell contains a very thin layer of solid on the bottom, and if the cell initially contains an appreciable quantity of solid, the vapour pressure should show an apparent decrease as the cell is emptied. In practice, no systematic variation was ever observed, indicating that under the present conditions the depth of solid in the cell was not an important factor. An alternative derivation of W (Bradley and Volans, *Proc. Roy. Soc.*, 1953, *A*, **217**, 515; Rossman and Yarwood, *J. Chem. Phys.*, 1953, **21**, 1406) gave a value between 0·95 and 1·0, depending on the values assumed for the evaporation coefficient and the effective area of the solid in the effusion cell. From a practical point of view, therefore, errors due to the use of the Whitman figures would not be more than a few units % and would have very little influence on the slope of the $\log_{10} p$–$1/T$ graph. Results were as follows :

Temp.	19·2°	23·2°	27·2°	31·2°	35·2°
Vapour pressure × 10⁴, mm. Hg	0·735	1·26	2·11	3·71	6·08

Calculation by use of regression equations showed that the vapour pressure (in mm.) can be represented by $\log_{10} p = -5201/T + 13{\cdot}66$, which leads to 23·7 kcal./mole for the heat of sublimation, with a standard deviation of 0·3 kcal.

To check the accuracy of the measurements, the vapour pressure of benzophenone (for which accurate values are known; Neumann and Völker, *Z. physikal. Chem.*, 1932, *A*, **161**, 33; Hartshorne and Bradley, personal communication) was determined over the same pressure range. The material used (B.D.H.) was crystallised from ethanol followed by vacuum-sublimation as for azoxybenzene, and had a melting range 47·9—48·2°. The measured vapour pressures, together with Neumann and Völker's values, were as follows :

Temp.	9·0°	17·0°	21·4°	25·3°
Observed v. p. × 10⁴ (mm. Hg)	0·74	2·24	3·92	6·04
Neumann's value × 10⁴ (mm. Hg)	0·71 *	2·14	3·89	6·46

* Extrapolated value.

The discrepancies are considered to be slightly greater than the experimental error, and indicate that the value of W should be a few units % higher than the Whitman figure in order to reduce the lower values, and that slight self-cooling occurred at the highest pressure. By using an effusion cell of the same dimensions but smaller orifice (radius 0·518 mm., Whitman W 0·976) the vapour pressure at 25·3° was found to be $6{\cdot}51 \times 10^{-4}$ mm., which supports the suggestion of self-cooling at this pressure with the larger-orifice cell. However, if the above results are used to calibrate the larger-orifice cell, the corrected azoxybenzene values lead to a heat of sublimation not greater than 24·9 kcal./mole, only 1·2 kcal./mole greater than that obtained when using the Whitman value of W. The heat of sublimation can therefore be given with confidence as 24 ± 1 kcal./mole. Measurements on liquid azoxybenzene between 37° and 49° gave $\log_{10} p$ (mm. Hg) $= -4361/T + 10{\cdot}97$, corresponding to a heat of vaporisation of 19·9 kcal./mole (standard deviation 0·13), and therefore a heat of fusion of *ca.* 4 kcal./mole.

DISCUSSION

Transformation under Red-light Conditions.—The transformation form II $\longrightarrow$ form I, in view of its strict linearity with time, independence of film thickness, and the occurrence of only slight spontaneous nucleation, has proved very satisfactory for kinetic measurements near room temperature under thin-film conditions. The average coefficient of variation of the rate is 11·7% (*i.e.*, on the basis of a rate = 100), a comparable figure in the sulphur work (Hartshorne, personal communication) being 11%, and can be considered good for this type of kinetic work. The low variance is considered to be due to (*a*) the high purity of the azoxybenzene, (*b*) the carefully standardised procedure for preparing and transforming the films, and (*c*) the fact that the total area of transformation at any one temperature was relatively large (about 30 cm.^{2} as compared with about 4·5 cm.^{2} for sulphur). Reasonable confidence can therefore be placed in the activation energy and pre-exponential factor derived from the rate measurements.

On the basis of an Arrhenius-type equation, the apparent activation energy is 17·9 kcal./mole (Fig. 3, line A). This is significantly less than the heat of sublimation of form II, *viz.*, 23 ± 1 kcal./mole, obtained on the reasonable assumption of 1 kcal./mole for the heat (q) of the transition II $\longrightarrow$ I: cf. $q = 0{\cdot}7$, 1·4, and 1·5 kcal./mole for benzophenone, carbon tetrabromide, and *n*-undecane respectively (Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, 1950). However, the indicated curvature at the high-temperature end of line A suggests that the expected maximum in the rate (observed with sulphur) might have been realised had it been possible to carry out rate measurements at temperatures nearer the theoretical transition point (T_0), which occurs above the m. p. of either form and where the rate of transformation would be zero. In view of the closeness of the m. p.s of the two forms, T_0 would probably occur at a temperature not higher than about 50°. An estimate of T_0 can be obtained as follows, the units of the vapour pressure p being mm. Hg. The equation for the solid–vapour curve of form I is $\log_{10} p = -5201/T + 13{\cdot}66$, and if it is assumed that $q = 1$ kcal./mole, the corresponding equation for form II is therefore $\log_{10} p = -4976/T +$ constant. The vapour pressure of form II at its m. p. (36·2°) can be obtained from $\log_{10} p = -4361/T + 10{\cdot}97$, the equation for the liquid–vapour curve, and hence the value of the constant found to be 12·95. The two solid–vapour curves can now be shown to intersect at 44°, which is the value of T_0. This value, in view of the small value of q, is subject to appreciable error, but the calculation does show that $q = 1$ kcal./mole is consistent with a value of T_0 between 40° and 50°. It is of interest therefore to consider the results for the present monotropic process in the light of the mechanism proposed by Hartshorne for the enantiotropic sulphur transformation. The latter is based on the difference in rates of escape of molecules from the two adjacent lattices and leads to the equation

$$\log_e \text{Rate} - \log_e\{1 - \exp[q(1/T_0 - 1/T)/\boldsymbol{R}]\} = -E/\boldsymbol{R}T + \log_e\tfrac{1}{2}A$$

where E and A are respectively the activation energy of escape and the temperature-independent factor of the rate of escape of molecules from the metastable lattice. In the case of sulphur, the plot of the left-hand side of the equation against $1/T$ did not give the required straight line except in the temperature range 0—30°, the corresponding value of E being close to 22·5 kcal./mole, which is the accepted value of the heat of sublimation of monoclinic sulphur. Hartshorne has shown, however, that over the whole range of measurements (0—80°) the deviations from the requirements of the theory can be accounted for by quite small variations in the activation energy of escape of molecules from the stable lattice. Applied to the present results, with $q = 1$ kcal./mole and $T_0 = 50°$ c, the above equation gives line *C* in Fig. 3, the slope coresponding to $E = 22{\cdot}5$ kcal./mole, which agrees well with 23 ± 1 kcal./mole, the heat of sublimation of form II. Variation of q from 0·5 to 2·0 kcal./mole or of T_0 from 50° to 40° c does not alter the value of E by more than 1 kcal. or substantially affect the fit of the points to a straight line. The value of A, calculated at 20°, is $7{\cdot}72 \times 10^{14}$. Theoretically, if application of Hartshorne's equation does in fact yield a straight line for *C* in Fig. 3, then line *A* should be slightly curved over its entire length. The curvature required (found by mathematical transformation of *C* back to *A*) is, however, very slight and the resulting curve is indistinguishable within the experimental error from the straight line *A*. Over a larger temperature range, the curvature would probably be more apparent as it is with sulphur. The same conclusion regarding activation energy was reached by Hartshorne *et al.* for *o*-nitroaniline (*J.*, 1935, 1860), but not for mercuric iodide (*J.*, 1938, 1636) where the activation energy was less than the heat of sublimation.

Calculations based on work by Burgers (*Proc. K. Ned. Akad. Wet.*, 1947, **50**, 719) and Mott (*Proc. Phys. Soc.*, 1948, **60**, 391) have shown (Hartshorne, *Discuss. Faraday Soc.*, 1949, **5**, 149) that for sulphur the thermal activation of one molecule with energy equivalent to the heat of sublimation leads to the transformation of *ca.* 10^7 molecules. By the same procedure, with use of the above value of A, or by application of the Polanyi–Wigner equation, the results for azoxybenzene give a value of *ca.* 10^9. This number of molecules corresponds to a unit of volume of *ca.* 3×10^{-13} cm.^{3}, which is within the range of the estimated size of a mosaic block. Hartshorne (*loc. cit.*; cf. Garner, *ibid.*, p. 194) has interpreted this behaviour on the basis of a mosaic block theory. It is thought that the transformation occurs with low energy of activation over small elements of volume (*i.e.*, mosaic blocks) and that a much higher energy is required to " bridge " adjacent blocks. If the bridges are formed by condensation of molecules from the vapour phase, the higher energy of activation will be approximately equal to the heat of sublimation and will determine the temperature coefficient of the transformation.

Further parallels to the sulphur transformation are as follows: (*a*) although the average rate of interface advance was constant under given conditions, microscopic examination showed that the transformation proceeded spasmodically over short distances, caused no doubt by lattice discontinuities of one kind or another, and that growing stable crystals did not change their orientation when crossing boundaries between differently oriented metastable crystals; (*b*) an estimate by Hartshorne's method (*J.*, 1951, 1113) of the vibration frequency of molecules from which bridges between mosaic blocks are formed was 10^5—10^6 times greater at 20° than the usual frequency of *ca.* 10^{13} sec.$^{-1}$ (with sulphur the discrepancy at 0° is 10^4 times); (*c*) from the vapour-pressure data, the rate of evaporation at 20° can be shown to be 10^5—10^6 times greater than that calculated from the Polanyi–Wigner equation: the corresponding discrepancy for rhombic sulphur is *ca.* 10^4 (*loc. cit.*).

Transformation after Irradiation with Ultra-violet Light.—The approximate doubling of the rate of the II $\longrightarrow$ I transformation after irradiation with ultra-violet light could be due to either a reduction in the activation energy of *ca.* 500 cal./mole, a quantity which is too small to be detected in the present instance (cf. Fig. 3) or an approximate doubling of the effective volume of the mosaic blocks. The fact that the increase in rate is more pronounced when irradiation is carried out with the films in the liquid rather than the solid state, suggests that the primary cause is a photochemical one. Since it is known (Badger and Buttery, *loc. cit.*) that irradiation by sunlight of azoxybenzene in organic solvents slowly leads to the formation of *o*-hydroxyazobenzene, it seems likely that minute amounts of this compound would be produced during the 15-sec. ultra-violet irradiation. Incorporation of the hydroxy-compound in the lattice of form II may then have been such as to influence the physical state of the films and favour the bridging of lattice discontinuities. In this connection, it has been observed that (*a*) red-light films, after being " annealed " at room temperature in the dark for 18 hr., were transformed at a much slower rate than normal, and (*b*) if the transition III $\longrightarrow$ II preceded the II $\longrightarrow$ I process in an otherwise standard red-light film, the II ⟶ I rate was much greater than normal. Both observations show that the physical state of the films had an important influence on the rate of transformation. However, attempts to reproduce the acceleration effect with known mixtures of azoxybenzene with *o*-hydroxyazobenzene failed. The destruction of the effect on frequent remelting of the films suggests, on the other hand, that the active photochemical product may be *cis*-azoxybenzene, which would revert to the normal form on melting (cf. *cis*-azo-compounds; Campbell, Henderson, and Taylor, *J.*, 1953, 1281). However, the existence of *cis*-azoxybenzene has not yet been established unambiguously (Gehrckens and Müller, *Annalen*, 1933, **500**, 296).

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