

A Kinetic Study on the n-Donor Complex Formation with Zinc-Phthalocyanine by Means of Quartz Crystal Microbalance and Electron Microscopy

Yoshio SAITO, Takashi KOBAYASHI, Natsu UYEDA and Eiji SUITO*

Received July 7, 1971

In order to elucidate the mechanism of the complex formation with respect to vacuum-condensed thin film of zinc-phthalocyanine in n-donor vapor, kinetic curves were obtained by means of quartz crystal oscillator as a very sensitive microbalance. It was found by the analyses of the curves that the total process involves three stages: the introductory process that follows the parabolic law, the transient process with a rapid rise in the molecular taking-up, and the final stage with a monotonous increase in vapor absorption.

The actual phenomena associated with the characteristic feature of a kinetic curve were examined by electron microscopy and diffraction to reveal that a preliminary growth of needle-like crystallites of zinc-phthalocyanine as the same α -polymorph as the original precedes the actual appearance of the nuclei of n-donor complex. The nucleation begins after the vapor molecules are absorbed by the capillary condensation in the networks of needle-like crystallites to exceed the necessary amount for the stoichiometry only by 20 to 30 %. The mechanism of the preliminary growth without changing the crystal form is discussed in comparison with that found in the case of the α - β transformation of Cu-phthalocyanine in organic suspension media.

INTRODUCTION

It has been found in previous investigations^{1,2)} that zinc-phthalocyanine forms additive complex with various amines and some other compounds which are often referred to as n-donors due to the non-bonding lone pairs located at nitrogen or oxygen atom. These complex compounds hold stoichiometric compositions with respect to the additive molecules and the molecular ratio is characteristic to the donor species as determined by means of differential thermogravimetry and X-ray powder diffraction. As to the molecular conformation, it was presumed by vibrational spectroscopy which covered rock salt and far infrared regions of the wave number that n-donor molecules are co-ordinated to the central metal ion of zinc-phthalocyanine by the non-bonding lone pairs.

Recently, the three dimensional Fourier analysis of X-ray diffraction³⁾ was applied to a single crystal of *n*-hexylamine complex for the precise determination of the actual molecular configuration which as a typical example proved the prediction about the co-ordination.

Although these results were all derived with respect to powdery or small crystalline materials prepared by suspending zinc-phthalocyanine in the indi-

* 斎藤 嘉夫, 小林 隆史, 植田 夏, 水渡 英二: Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

vidual n-donors as the dispersion media, it was also found that the same complexes can be formed in vapor of the same n-donors. The most striking feature can be well observed when a vacuum-condensed thin film is placed in the vapor. The original transparent blue film of zinc-phthalocyanine rapidly changes its color into greenish blue apparently indicating the formation of homogeneous film of a corresponding complex.

The present investigation has been attempted with respect to such a vapor-thin film system in order to elucidate the mechanism of complex formation by the use of a quartz crystal oscillator as an extremely sensitive microbalance⁴⁻⁶⁾ to measure the vapor absorption kinetics and also by the co-ordinated operation of the electron microscope to observe the crystal alteration and subsequent growth in the course of the complex formation.

EXPERIMENTAL

The quartz crystal used here for the microbalance element is a disk of AT-cut and the central circular part of 10 mm across is 1/3 mm thick whereas the surrounding part is tapered off toward margin. The characteristic frequency which is dependent on the crystal thickness was controlled to be 5 MHz by the vacuum deposition of silver electrodes on both sides. The frequency shift Δf due to the variation in the effective mass thickness Δm per unit area is given by the following relationship:

$$\Delta m = -\frac{d \cdot \rho}{f_0} \Delta f = -\frac{N \rho}{f_0^2} \Delta f, \quad (1)$$

where f_0 , d and ρ are the fundamental frequency, the thickness and the density associated with the element respectively, and N is often referred to as the frequency constant. Since the fundamental frequency is 5 MHz, the theoretical sensitivity as the microbalance is expected to be 1.77×10^{-8} g/cm²/Hz. For the practical operation, however, a calibration curve was constructed by measuring the frequency shift Δf with respect to various amounts of vacuum-condensed zinc-phthalocyanine. The precise amount of the deposit was colorimetrically determined by dissolving in a definite amount of pyridine as the solvent of the phthalocyanine film deposited on a glass plate of a known area which was placed at the same distance from the evaporation source as that of the quartz oscillator plate. The standard solutions were prepared in an ordinary way by the use of powdery zinc-phthalocyanine and pure pyridine. With the resulted calibration curve, the lineality and the expected sensitivity are guaranteed in the frequency range examined here. The frequency shift Δf is measured with a digital frequency counter as the difference in the frequencies between a reference oscillator and the microbalance element as shown in the block diagram of Fig. 1. The original frequency difference inevitably existing at the beginning of experiment was always recorded and cancelled off the actual frequency shifts measured in the course of the total process.

The absorption kinetics was studied with thin films of zinc-phthalocyanine deposited on the crystal oscillator itself. The sample of zinc phthalocyanine was

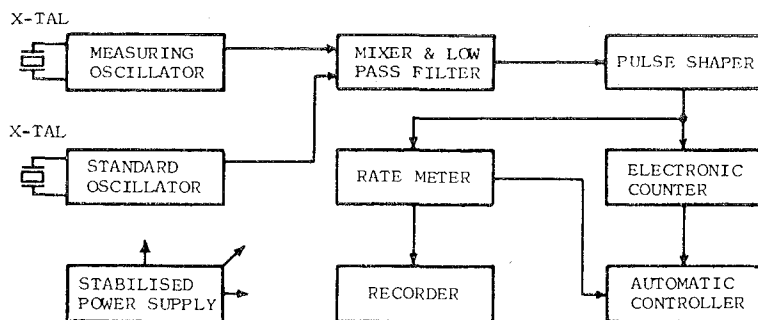


Fig. 1. Block diagram of the quartz crystal microbalance.

synthesized and purified as reported in the previous paper.¹⁾ The evaporation was carried out in a vacuum vessel. The quartz crystal oscillator is mounted to a metal rod penetrating into the vacuum vessel through a rotatable seal so that the crystal plate can be turned around from the outside keeping its diameter coincide with the rod axis.

The evaporation source equipped with a coiled tungsten wire as a heater on which powdery zinc-phthalocyanine is directly applied is located about 10 cm apart from the oscillator. As widely accepted, zinc-phthalocyanine is very thermostable and sublimated at about 500°C *in vacuo*. The heating current of the furnace was carefully controlled and the rate of condensation was monitored to keep a constant value as far as possible with the measuring oscillator itself, the surface of which was so oriented that the flux of the impinging molecules was normal to the plate face. Turning around the oscillator plate by 180°, the films were prepared on both sides of the plate with an exactly equal mass thickness ranging 0.01 to 0.001 mg/cm² under the rate of condensation of 1 µg/cm²/sec. in a vacuum of about 10⁻⁷ Torr.

The n-donors used as the vapor to react with the films are pyridine in most cases and others such as *n*-hexylamine and piperidine for comparison. Each vapor was led into the vessel, after the main cut-off valve to the evacuating system was closed, through a glass valve from a reservoir of the liquid n-donor with upper space evacuated beforehand by freezing the solvent with liquid nitrogen. Since the experiments were carried out at room temperature, the vapor pressure was regarded to be equal to the value tabulated in standard references.⁷⁾ As will be seen later, the period of the main reaction was mostly within an hour, the room temperature was considered almost constant.

The specimens for the electron microscopy were prepared by evaporating zinc-phthalocyanine on the specimen grid covered with thin vacuum-deposited carbon films, under the same condition of the mass thickness as well as the rate of condensation. The reaction was performed in the same vacuum vessel by placing the specimen grid one by one subsequently exposing it to the n-donor vapor. When the necessary time was elapsed, the specimen was quickly taken out by breaking the vacuum after a prompt evacuation of the vapor. The specimens were examined with JEM-7A Electron Microscope, operated under an ac-

celerating voltage of 100 kV. The identification of the crystals was performed by high resolution electron diffraction. The period to terminate the reaction with each specimen was determined selecting the characteristic points on the kinetic curves of the gas absorption measurement by the quartz crystal microbalance.

RESULTS

1. Absorption Kinetics

When the net amount of the frequency shift was plotted against the time in second, it was found that the curves obtained showed rather complicated behavior although the frequency shift increased with time as shown in Fig. 2. The curves collected here are for a system of zinc-phthalocyanine films with thickness ranging 0.004 to 0.07 mg/cm² and pyridine as the n-donor under a pressure of 16 Torr. at 21°C. As apparent from the curve, the frequency shift, that is, the amount of pyridine molecules taken up by the film, are monotonously increased at the first stage up to 300 to 400 seconds and show rapid increase until they fall into another monotonous almost linear increase with rather slow gradient.

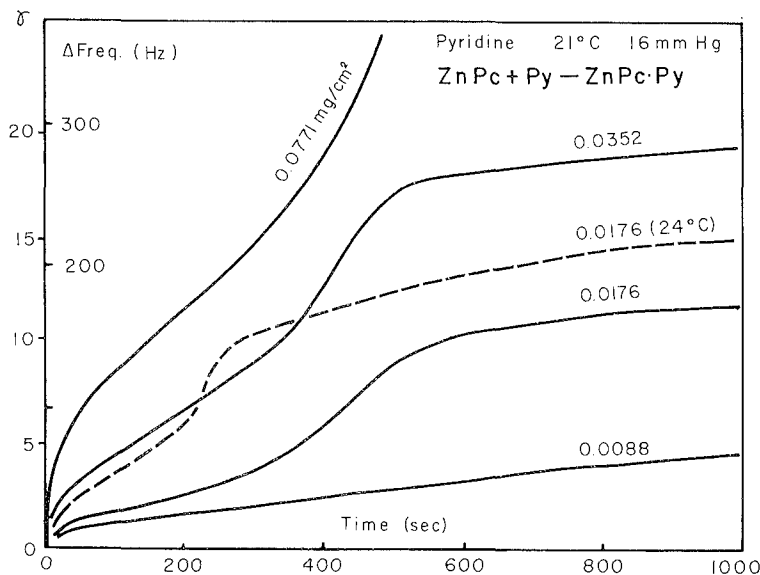


Fig. 2. Time dependence of vapor absorption. (Zinc-phthalocyanine-pyridine)

When the curves are plotted by the log-log scale as shown in Fig. 3, these characteristic behaviors can be understood more distinctively. It is interesting to note that the curves, particularly those for thicker films, would almost coincide with one another if parallel translation is applied to them. Generally speaking, the curves consist of three parts: the initial and final stages where the curves are regarded as almost linear and the intermediate stage where $\log \Delta f$ shows rapid increase with $\log t$. It was revealed by numerical analyses that the linear part at the earlier stage represents the following kinetic equation:

$$\Delta m = k \cdot t^{0.5}, \quad (2)$$

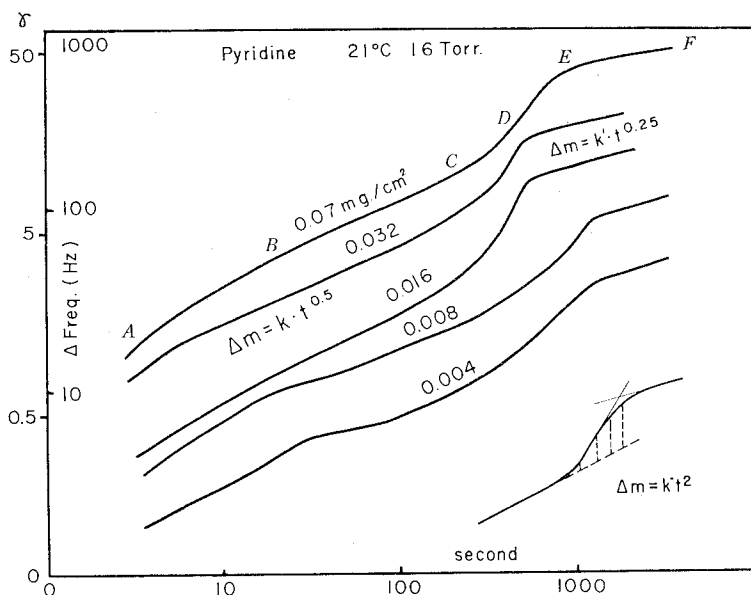


Fig. 3. Kinetic curve for vapor absorption in log-log scale. (Zinc-phthalocyanine-pyridine)

where Δm is the amount of vapor taken up and k is a constant. On the other hand, another linear part at the final stage, having slower gradient than the former one, defines the following equation:

$$\Delta m = k'' \cdot t^{0.25}, \quad (3)$$

where k'' is a rate constant.

As for the intermediate stage where the curves show rapid increase, no reasonable equations could be ascribed to. However, if it is assumed that in this stage a different phenomenon is overlapped to the still continuing main reaction of the first stage, the extra increment $\Delta m'$ of the taken-up can be estimated by subtracting the expected increment given by the extrapolation of Eq. 2. The increment $\Delta m'$ was found to follow an equation with another constant k' expressed as:

$$\Delta m' = k' \cdot t^n, \quad (4)$$

where n is nearly equal to 2.

Figure 4 shows similar kinetic curves obtained with respect to *n*-hexylamine and piperidine, having vapor pressures of 5.6 and 2.3 Torr. respectively at 21°C as the reaction temperature. The film thickness was controlled so as to be almost equal for both *n*-donors. Although two different thicknesses were tried, the tendency is quite similar as for each amine vapor. Taking it into account that the vapor pressure is much lower for *n*-hexylamine than the other, the affinity of the former is likely to be stronger than that of piperidine, since the intermediate stage of the rapid rise is reached much earlier than the other irrespective of the film thickness.

Some notable data obtained from the curves are collected in Table 1 in regard

Kinetic Study on the n-Donor Complex Formation

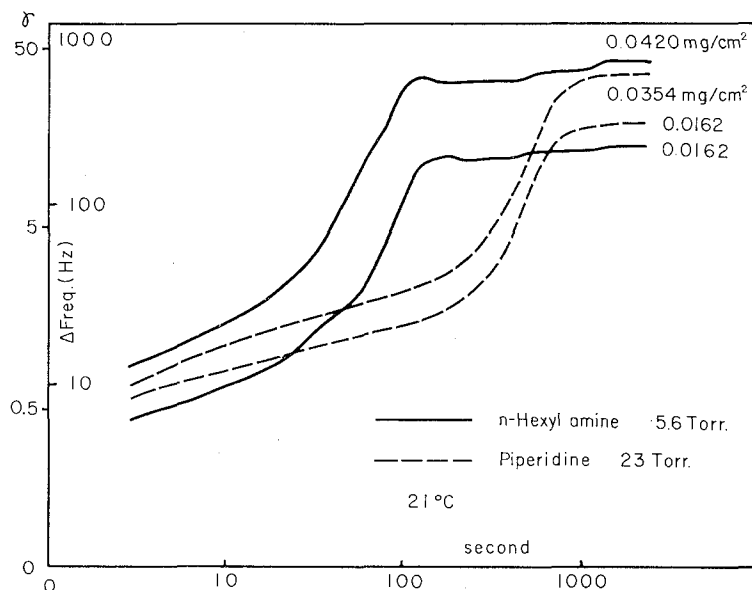


Fig. 4. Comparison of absorption kinetics between piperidine and *n*-hexylamine.

Table 1. Molecular Ratio of Absorbed Amine to Matrix Film.

n-Donors	Zn-phthalocyanine M_p ($\mu\text{g}/\text{cm}^2$)	Amine vapor M_s ($\mu\text{g}/\text{cm}^2$)	R_{obs} (M_s/M_p)	R_{calc} (M_s/M_p)	Molecular ratio	R_{obs}/R_{calc}
pyridine	3.41	0.77	0.224	0.136	1 : 1	1.69
	6.80	1.09	0.160			1.18
	13.6	2.38	0.175			1.29
	28.4	4.83	0.170			1.25
	59.8	10.04	0.168			1.24
piperidine	13.8	4.25	0.380	0.284	1 : 2	1.34
	29.1	9.35	0.311			1.89
<i>n</i> -hexylamine	13.6	3.40	0.250	0.262	1 : 1.5	0.96
	34.2	9.54	0.279			1.06

to the amount of the taken-up n-donor vapor relative to the amount M_p of the matrix film. For the practical convenience, the amount of vapor M_s for comparison was defined at the intersection of the two extrapolations of the last two stages. In the table, the ratio R_{obs} ($=M_s/M_p$) is listed for the comparison with corresponding ratio R_{calc} based on the stoichiometric molecular ratio of each complex.

2. Electron Microscopy and Diffraction of Crystal Alteration

Although the actual phenomenon which corresponds to each of these stages cannot be presumed from the mere analysis of the curves, more tangible information would be available through electron microscopy as far as the structural change is concerned.

Figure 5 is a series of electron micrographs of zinc-phthalocyanine films which suffered the crystal alteration due to the complex formation with pyridine at 21°C when the film thickness was controlled to be 0.06 mg/cm². A general survey of these photographs in sequence indicates that the feature of crystal variation is

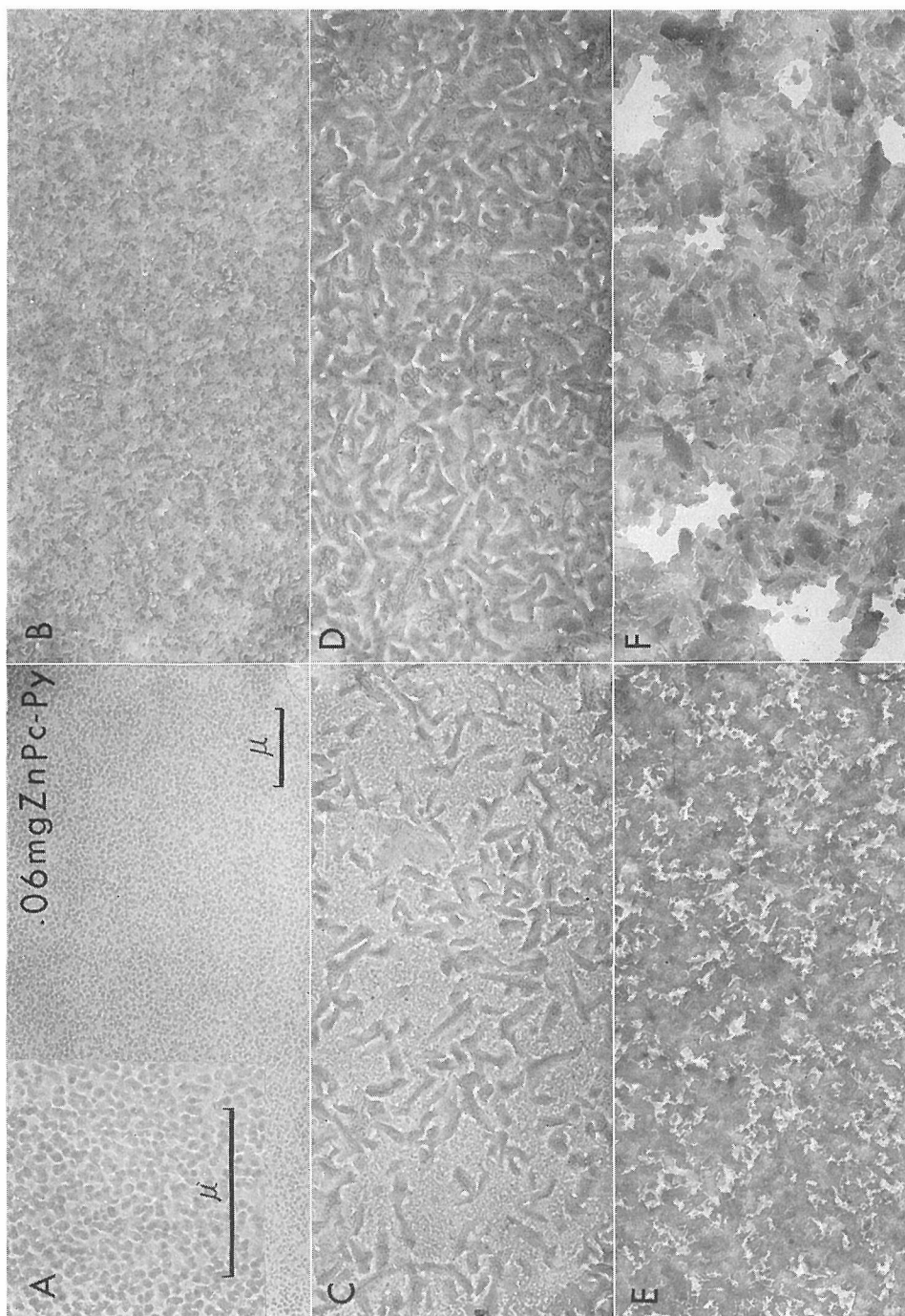


Fig. 5. Serial electron photomicrographs for crystal alteration.

not simple in accord with the complicated behavior presumable from the kinetic curves. The six photographs in Fig. 5, A through F were taken so that they corresponded to those characteristic points indicated by the same sequence of letters, A through F, inscribed on the typical kinetic curve shown in Fig. 3.

The original film consists of small crystallites whose average size is about 600 Å across as shown in Fig. 5, A. The electron diffraction patterns reproduced in Fig. 6, a which corresponds to Fig. 5, A, indicates that the crystal modification is the α -polymorph, although the Debye-Scherrer rings are all diffuse due to the small size of the crystallites and probably to various lattice defects involved in them.

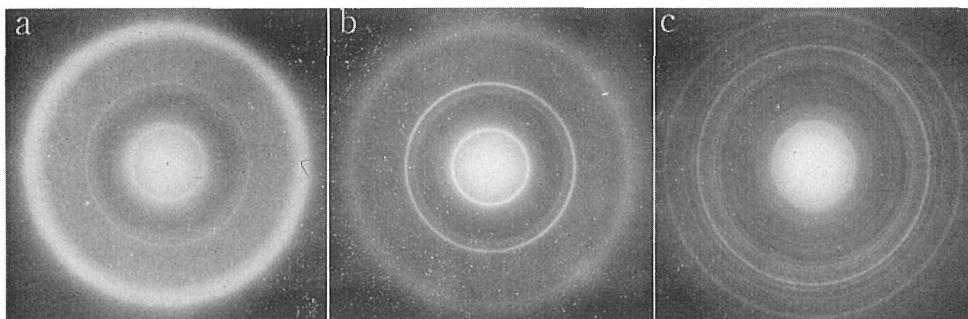


Fig. 6. High resolution electron diffraction patterns to indicate the crystal alteration.

The particle size gradually increases with the lapse of reaction time as apparent from the series of photos in Fig. 5, B through D. The most striking feature appears around the points C to D where the curve goes into the rapid rise in the taken-up of n-donor vapor. The sporadic appearance of spindlelike crystallites which are observable in the photo C have grown into better defined needle crystallites which, assuming various orientations in the film plane as shown in D, form a two dimensional net structure as a whole.

In spite of such a remarkable change in the crystal appearance, it has been revealed by the electron diffraction that the crystals are all identified to be the α -form and no indications of the complex crystal are detected in the pattern. This means that the phenomenon which takes place in the earlier stage is simply a crystal growth in the state of the α -form as seen from the sharpening of the diffraction rings such as seen in Fig. 6 b as well as in the electron micrographs.

It is around the point E that the nuclei of the complex can be clearly observed. In Fig. 5, E, small crystallites with a different habit from the foregoing ones begin to appear in the matrix leaving apparent voids among them. The corresponding electron diffraction, Fig. 6, c is also quite different from the former patterns of the α -form, suggesting the formation of the complex. As the time elapses, the recrystallization into well defined complex crystallites seems to occur taking up more donor molecules from the vapor as indicated by the Photo F and corresponding behavior of the kinetic curve.

DISCUSSION

The quartz crystal oscillator is regarded as a very sensitive microbalance

since the frequency shift of a few Hz can indicate the thickness change which corresponds even to a monomolecular layer of adsorbed gas such as oxygen or nitrogen so far as a theoretical estimation is concerned. In practice, however, it has an inherent drawback that the frequency shift is dependent on the RF current fed to the crystal oscillator. Since this is considered to be mainly due to the slight temperature rise of the oscillator which in turn affects the equilibrium state of the gas adsorption, the crystal current was carefully controlled to keep a constant value through the whole experiments.

It has been revealed that the actual reaction of the complex formation is not so simple as for the nuclei of the new crystal to appear from the outset of the total process, as clearly seen from the kinetic curves in good accord with the results of the serial electron microscopy. In fact, preliminary growth of zinc-phthalocyanine crystallites takes place in advance keeping its crystal structure as the α -polymorph. A similar effect is often observed in other cases where polymorphic transformation from the α - to the β -form takes place with respect to various metal phthalocyanines as reported in the previous papers.^{8,9)} It was found that a preliminary growth of the α -form gives rise to a needle-like crystallites of the α -form in advance of the appearance of the final β -form. These findings are, however, associated with powdery phthalocyanines suspended in organic media or the vacuum condensed thin films dipped in the same media. Although the solubility of these compounds in the media used is generally very small, it is an essential prerequisite for the formation of new nuclei that a crystallite should be dissolved or, at least, its lattice should be loosened to some extent by the surrounding solvent. In the present case, however, the films are exposed to the vapor molecules of *n*-donor instead of being dipped in the solvent. The present films are continuous in appearance, but, in fact, they are composed of small crystallites of 600 Å across. With such film configuration, the adsorbed vapor molecules would diffuse through the grain boundary to surround the individual particles. This presumption is well supported by the fact that the kinetic curves follow the parabolic law of Eq. (1), which can be derived on the basis of a mechanism controlled by the linear diffusion of gas molecules through the matrix of the heterogeneous reaction. The crystal lattice may be loosened and dissolved into the molecular films of *n*-donor. It is reasonable to consider that the complex molecules may be formed locally, but, in fact, the recrystallization and growth of the original form precedes the actual formation of the stable nuclei of the complex crystal, which are likely to appear after a good enough complex molecules are formed through fluctuation. In this case, some of the α -form crystallites, probably the larger ones, act as the nuclei existing already in the system so that no other crystals such as the β -form and the complex appear at this stage even though they are more stable than the original α -form.

Figure 7, a is to show the planar configuration of zinc-phthalocyanine molecule which is covered with π -electron orbitals. The crystal of the α -form as well as that of the β -form assumes a needle-like crystal habit mainly owing to the planar configuration with π -electrons which give rise to a strong periodic bond chains¹⁰⁾ in the crystal resulting in the formation of columns of stacked molecules

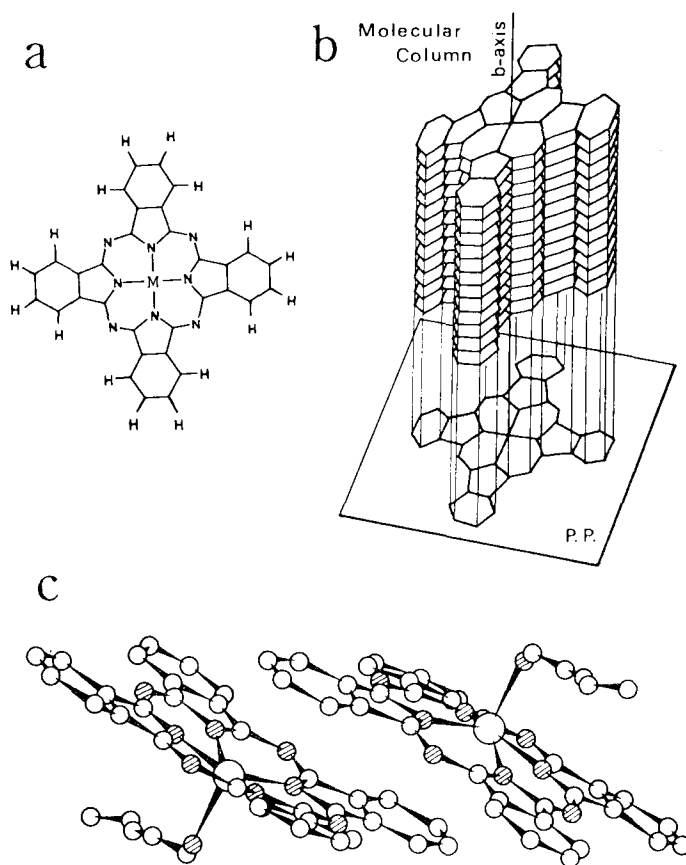


Fig. 7. Molecular and crystal structures of zinc-phthalocyanine and its complex.
 a: Zinc-phthalocyanine, b: Molecular stacking of the α -polymorph, c: Co-ordinated structure of *n*-hexylamine complex.

as illustrated in Fig. 7, b. When these needle-like crystals grow to form two dimensional networks as seen in Fig. 5, D, the capillary condensation would take place among the crystallites, particularly at the cross-links of the needles. This may well explain the rapid rise in the kinetic curves at the intermediate stage.

It may be clear from Table 1 that the amount of the taken-up molecules at the beginning of the final stage is about 20 to 30 % excess of the amount necessary to hold the stoichiometry of the complex molecules. Even with such a small excess amount of n-donor molecules absorbed by the film, the probability of forming the additive complex molecules seems to increase so that the nuclei of the new crystallites appear in the state of divided particles as apparent from Fig. 5, E. The further increase in the absorbed vapor may be effectively used for the recrystallization into much well defined state as exhibited in Fig. 5, F.

As reported in the previous paper,¹⁾ the complex crystals can be formed not only from the α -form but also from the β -form as well. The β -form is more stable than the α -form with an energy difference of about 2.4 kilocalories as measured by Beyon and Humphries¹¹⁾ with respect to Cu-phthalocyanine. Although

the heat of formation of n-donor complex has not been measured, it can be presumed that the complex may be even more stable than the β -form. The n-donor molecules are rigidly co-ordinated to the central zinc ions as illustrated in Fig. 7, c which has been determined by three dimensional Fourier analysis of X-ray diffraction with n-hexylamine complex as will be reported in detail elsewhere.³⁾

When these factors taken into account, it is rather impressive to note that the complex formation never starts from the outset of the total process but a preliminary growth of the original crystal precedes in the same manner as that of the α - β transformation. It should be also noted that the recrystallization can occur even with the existence of considerably small amount of absorbed solvent molecules. This phenomena may be interpreted in terms of the successive interchange of the individual n-donor molecules between two adjacent zinc-phthalocyanine molecules resulting, to the effect, in the separation of the phthalocyanine molecule from the lattice of a "dissolving" crystal and their subsequent diffusion to the more stable nuclei to grow into a needle-like crystallite of the existing α -form.

On the other hand, the recrystallization of the product complex seems to be an essential process of such a heterogeneous reaction. As shown in Fig. 8, a more striking feature was found in the case of dimethyl sulfoxide (DMSO) complex formed with a zinc-phthalocyanine film vacuum-deposited on a cleaved face of KCl single crystal. The original continuous film which was similar in appearance to that shown in Fig. 5, A, was divided into domains surrounded by well defined crystals. The inside small grains with irregular contrasts are identified to be the imperfect complex crystallites as indicated by the selected area diffraction

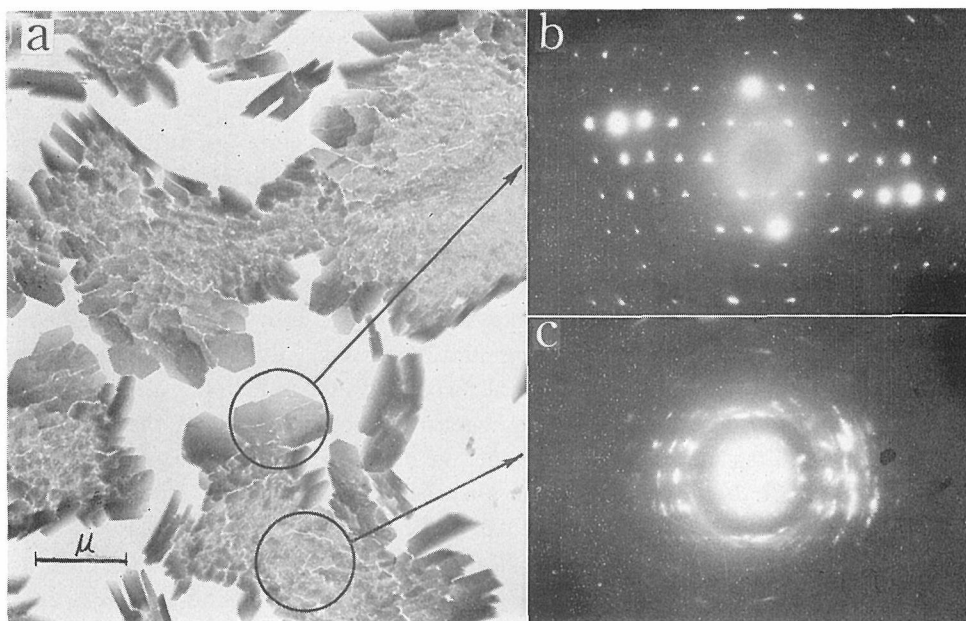


Fig. 8. Electron photomicrographs and selected area diffraction of DMSO complex under recrystallization.

tion. The marginal crystals which assume characteristic habits are apparently resulted from the recrystallization as indicated by the regular single crystal pattern of the selected area diffraction. Since the original film was continuous, the vacant backgrounds suggest that the molecules of zinc-phthalocyanine that covered the same area diffused over a considerable distance to reach the domains for the formation of the complex crystallites leaving these vacancies behind. Then, it is considered that the absorbed n-donor molecules, DMSO in this example, must have acted somehow as the media for the diffusion of such large molecules as phthalocyanine.

On the basis of these observations, it seems reasonable to consider that the absorbed molecules through capillary condensation, even though the total amount is only a little more than that necessary to hold the stoichiometry, behaves as if the film itself were dipped into the liquid phase of the n-donor. In other words, the n-donor molecules play the role of the intermediary of such a dynamic behavior of the large phthalocyanine molecules.

More quantitative work would be necessary, however, to reach a better understanding of the actual molecular movement, particularly in respect to both recrystallization processes.

REFERENCES

- (1) T. Kobayashi, N. Uyeda and E. Suito, *J. Phys. Chem.*, **72**, 2446 (1968).
- (2) T. Kobayashi, F. Kurokawa, N. Uyeda and E. Suito, *Spectrochim. Acta*, **26 A**, 1305 (1970).
- (3) T. Kobayashi, N. Uyeda, E. Suito, T. Ashida and M. Kakudo, *Bull. Chem. Soc. Japan*, **44**, 2095 (1971).
- (4) R. M. Mueller and W. White, *Rev. Sci. Instr.*, **39**, 291 (1967).
- (5) W. H. Lawson, *J. Sci. Instr.*, **44**, 917 (1967).
- (6) G. Sauergrey, *Z. Phys.*, **155**, 206 (1959).
- (7) Chem. Soc. Japan, *Kagaku Binran*, p 561, Maruzen (1966).
- (8) E. Suito and N. Uyeda, *Proc. Japan Acad.*, **33**, 398 (1957).
- (9) E. Suito and N. Uyeda, *Kolloid-Z.*, **193**, 97 (1963).
- (10) P. Hartman, *Acta Cryst.*, **8**, 521 (1955).
- (11) J. H. Beyon and A. R. Humphries, *Trans. Farad. Soc.*, **51**, 1065 (1955).