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The Pyrolysis and Thermochromism of the Crystalline Powder of Dianthraquinone

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The crystalline powder of dianthraquinone changes its color from yellow to green when it is heated above 250°C. A heat-treated powder of a green color exhibits an ESR absorption, the line width of which is about 7 gauss, and the g-value, 2.0032. The intensity of the ESR absorption was studied as a function of the temperature of heat-treatment and the heating time. The activation energy for the formation of the paramagnetic species is estimated to be 74 kcal./mol. The X-ray diffraction patterns of heat-treated specimens indicate that a marked disorder is produced in the crystal structure by the heat treatment and that, finally, the dianthraquinone crystal becomes an amorphous solid. A close correlation can be found between the intensity of ESR absorption and the structural change. Polymerization occurs at higher temperatures and results in the formation of a dark green solid insoluble in organic solvents. It is suggested that the initial process of these thermal changes is associated with the thermochromism of dianthraquinone.

It is well known that a solution of dianthraquinone shows a thermochromism, namely, a reversible change of color from yellow to green, as its temperature is raised.[1-3] Nielsen and Fraenkel found that the solution shows an electron-spin-resonance (ESR) absorption when it is in the green-colored state at an elevated temperature.[4] Thus, it is suggested that the thermochromism of dianthraquinone is due to the thermal equilibrium between two isomeric forms of the molecule, in which the high energy form is in a biradical state or a triplet state. The molecular structure of this high energy form has been a matter of discussion for a long time, different models have been proposed by several investigators.[5-8]

A crystalline powder of dianthraquinone shows a similar color change at elevated temperatures.[1] The color changes from yellow to green when it is heated to about 250°C. In this case, however, the change is not reversible, and the powder remains in the green colored state as the temperature is lowered. According to Mayer,[1] the original color can be completely recovered by recrystallization. Matsunaga[9] showed that the diamagnetic susceptibility of the dianthraquinone powder appreciably decreases when it is treated for about 1 hr. at temperatures above 240°C. This suggests the formation of paramagnetic species, which is in agreement with the observation of ESR absorption by Nielsen and Fraenkel.[4] According to Matsunaga,[9] however, the change caused by the heat treatment is by no means reversible, and some kind of polymerization seems to occur during the heat treatment, which makes it hard to dissolve the heat-treated solid in organic solvents. He concluded, therefore, that the color change of the dianthraquinone powder is not due to the thermochromism, but to a chemical reaction or a pyrolysis.

Extensive investigations have been made into the evolution of paramagnetism in the process of the pyrolysis of various organic materials.[10-13] When we compare the behavior of dianthraquinone with the pyrolysis of a usual organic compound, the initial variation in ESR absorption with the heat-treatment at temperatures below 300°C is considerably different. It seems of interest to see, therefore, whether this peculiarity in the thermal change of dianthraquinone powder is associated with the thermochromism or not. In the present study we have investigated the ESR absorption and the X-ray diffraction on the heat-treated powder of dianthraquinone in order to elucidate the nature of the thermal change.

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Experimental

Dianthraquinone was synthesized from the commercial anthraquinone,⁹⁾ and purified by recrystallization repeated three times.* The dianthraquinone powder was heat-treated in an atmosphere of ambient nitrogen by means of a small electric furnace. The heat-treatment temperature (HTT) was varied in the 200—300°C range. The powder was heat-treated while sealed in a glass capillary to facilitate ESR measurement. The X-ray diffraction was examined by using a X-ray diffractometer, Geigerflex (Rigaku Denki Co.), with Cu$K\alpha$ radiation, and the ESR spectrum, by means of a Hitachi MPS-1 ESR Spectrometer. All measurements were made at room temperature.

Results and Discussion

At a low HTT, below 200°C, the dianthraquinone powder changes little in color, even if it is heated for several hours. No ESR absorption can be detected with a heat-treated powder in this case. The color change becomes appreciable, however, as the HTT exceeds 240°C. After a 25 min. treatment, the color becomes pale green at 250°C and green at 270°C. The ESR absorption can be observed with a green-colored powder, as has been reported by Nielsen and Fraenkel. Its intensity increases parallel with the color change, the absorption being weak for a pale green powder and strong for a green one. The spectrum consists of one broad line without a structure, the line width being about 7 gauss and the g-value, 2.0032. The spin concentration estimated from the intensity of the ESR absorption is given in Table I for the powders treated for 25 min. at several temperatures. In the 200—300°C, range, the spin concentration increases as the temperature is raised, but it decreases in the 300—400°C range. If the HTT is raised above 400°C, a carbonaceous solid of a black color is formed, and the intensity of ESR absorption increases again. The change which occurs above 500°C is not different from the one found for the pyrolysis of usual organic solids.

TABLE I. THE SPIN CONCENTRATIONS OF THE HEAT-TREATED POWDER OF DIANTHRAQUINONE

HTT °C	Spin concn., spins/g. Heated for 15 min. in nitrogen	Heated for 15 min. in air
230	0.84×10^{17}	1.06×10^{17}
240	1.73×10^{17}	1.85×10^{17}
252	1.11×10^{18}	1.72×10^{18}
270	$7.6\ \times10^{18}$	1.36×10^{19}

The spin concentration is dependent not only on the HTT but also on the length of heat treatment. Its variation with time is shown in Fig. 1. The spin concentration increases at first linearly with time, but reaches a maximum and decreases afterward. The results shown in Fig. 1 evidently suggest that two different processes are involved in the thermal change observed here. The one is the formation of paramagnetic species, while the other is a reaction that results in the disappearance of the paramagnetism.

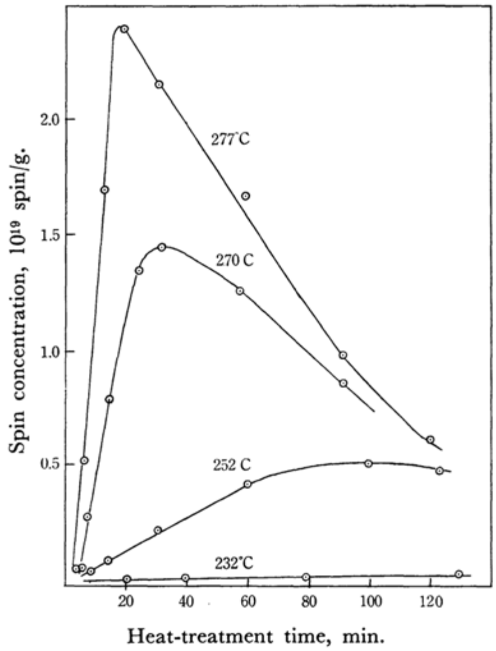

Fig. 1. The variation of spin concentration on heat-treatment of the dianthraquinone powder.

The pyrolysis of an aromatic compound usually begins at a temperature about 400°C. The paramagnetism appears at the same time, and increases with the progress of the carbonization. When the starting material contains some free radicals, however, the pyrolysis begins at lower temperatures because of the instability of the free radicals. This causes an initial decrease in the spin concentration at temperatures about 300°C.¹²⁾ In the region of much higher HTT values, however, the dependence of the spin concentration on the HTT is similar to that for the pyrolysis of usual organic compounds. The behavior of dianthraquinone powder seems similar to the case described above except that the free radicals are not present from the beginning, but are formed in the first step of the thermal change.

It should be mentioned here that the ESR absorption of the heat-treated dianthraquinone is little affected by the oxygen. No appreciable change can be found in the intensity as well as in the line width of the ESR spectrum when a specimen prepared in vacuo or in nitrogen is exposed to air. The difference in the spin concentration

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* Solvesso-100 (Standard Vacuum Oil Co.) was used as the solvent.

is quite small even if dianthraquinone is heat-treated in air instead of in nitrogen, as is shown in Table I.

The X-ray diffraction patterns of several heat-treated specimens are shown in Fig. 2. The diffraction peaks due to the dianthraquinone crystal are reduced in their intensity by the heat-treatment, and a diffuse scattering appears in the background. The intensity of the diffuse scattering increases with the progress of the thermal change. A dark green solid formed by the one-hour treatment at 270°C shows a diffraction pattern consisting only of diffuse scattering, like amorphous carbons. No diffraction peak associated with a new crystalline phase appears in the HTT range studied here. We can conclude that the heat treatment causes a marked disorder in the crystal lattice of dianthraquinone, finally resulting in the formation of an amorphous solid.

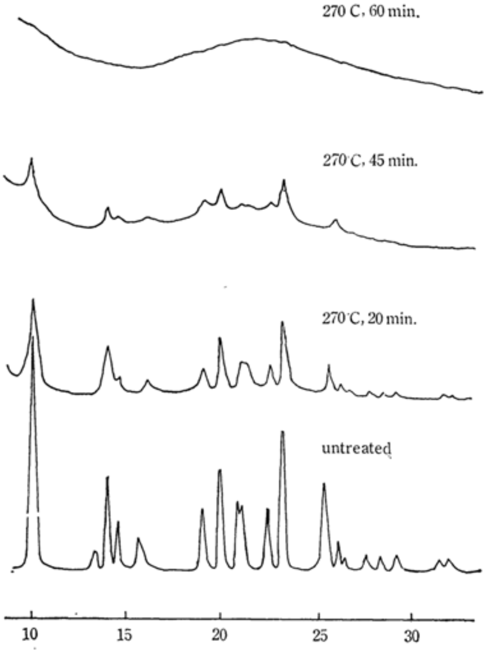

Fig. 2. The X-ray diffraction patterns of the heat-treated powders of dianthraquinone.

The ratio of the intensity of the crystalline diffraction to that of the diffuse scattering can be a measure of the crystallinity. For the value to represent the crystallinity of a heat-treated powder of dianthraquinone, we shall define here a quantity, K, by the following equation;

$$K=\int_{15^\circ}^{30^\circ} I_C \mathrm{d}(2\theta) \bigg/ \int_{15^\circ}^{30^\circ} I_D \mathrm{d}(2\theta) \qquad (1)$$

where I_C is the intensity of the crystalline diffraction; I_D, that of the diffuse scattering, and 2θ, the diffraction angle. The variation of K with the heat-treatment time is shown in Fig. 3.

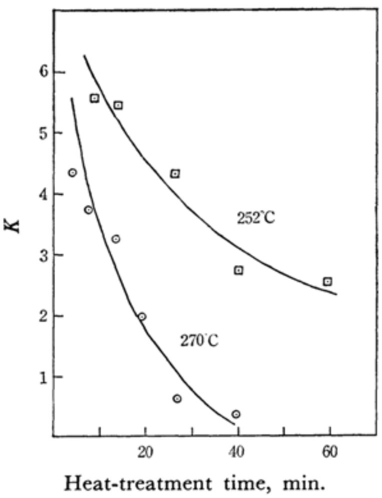

Fig. 3. The change in the crystallinity of dianthraquinone powder on heat-treatment.

In Fig. 4, the spin concentration, as determined from the ESR absorption, is plotted against the value of K. Interestingly, the points fall on a single curve in spite of the difference in the HTT. This means that the formation of the paramagnetic species and the change in the crystal structure are directly related to each other.

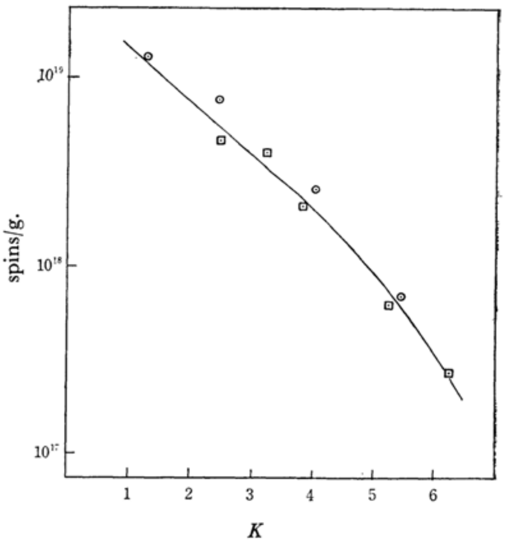

Fig. 4. The relation between the spin concentration and the crystallinity.
⊡ 252°C ⊙ 270°C

The pale green powder obtained by a short heat treatment at a low HTT can be dissolved in several organic solvents, and the original yellow color can be recovered by the recrystallization. However, a dark green powder prepared by a long treatment at 270° is insoluble in organic solvents; this is in agreement with the observation reported by Matsunaga. Between these two extremes, there is an intermediate state where the heat-treated powder is partialy soluble. We can extract unreacted dianthraquinone from a green specimen by treating it with a solvent. In this stage of thermal change, the dianthraquinone powder gives a diffraction pattern consisting of the diffraction peaks due to dianthraquinone and a diffuse scattering, but if dianthraquinone is extracted from it, the residue shows only a diffuse scattering similar to that of the dark green solid. Therefore, the main part of the insoluble component seems to be the product of polymerization. Suppose that the evolution of the paramagnetism is entirely due to the polymerization of dianthraquinone; the residue of the extraction may then be expected to have a higher spin concentration. However, the spin concentration after the extraction of dianthraquinone is a little smaller than that before the extraction. For example, the powder treated for 25 min. at 270°C originally has 13×10^{18} spins/g., but it has 4×10^{18} spins/g. after the extraction of the unreacted dianthraquinone. It seems that the paramagnetism is associated not only with the products of polymerization, but also with dianthraquinone molecules. Presumably the initial evolution of the paramagnetism is due to the formation of dianthraquinone molecules in a metastable triplet state, as it is in the case of thermochromism in the solution.

We can estimate the activation energy required for the formation of the paramagnetic species in the dianthraquinone crystal by using the experimental data obtained on the ESR absorption. As is shown in Fig. 1, the spin concentration of the heat-treated dianthraquinone at first increases linearly with the heat-treatment time. This can be fitted to a kinetic equation of the first-order reaction. We estimated the apparent rate constant, k, at several HTT value by assuming Eq. 2:

$$\mathrm{d}n/\mathrm{d}t = kN \tag{2}$$

where n is the spin concentration, and N, the number of molecules per gram. If the logarithm of k is plotted against the reciprocal of HTT, a straight line can be obtained, as is shown in Fig. 5; the activation energy can thus be estimated to be 74 kcal./mol. On the other hand, the energy difference between the two isomeric forms has been experimentally determined to be 3.4 kcal./mol. for the thermochromism in the solution. Therefore, the observed activation energy for the formation of paramagnetic species in the solid state is too large to be simply attributed to the energy difference between the two isomeric forms of the thermochromism.

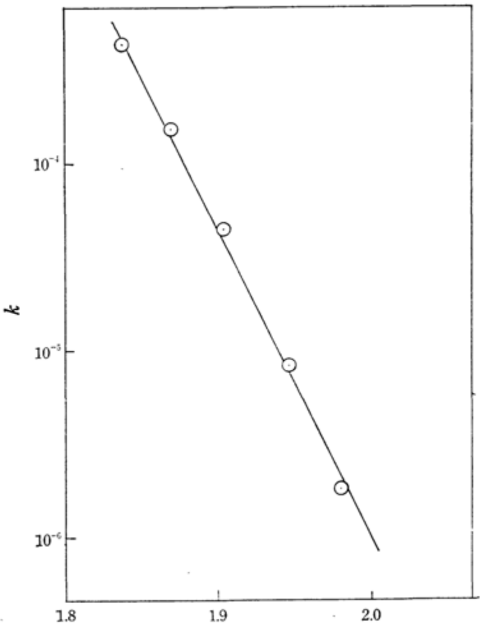

Fig. 5. The plot of $\log k$ against $(1/T)$.

According to the model given by Hirschberg and Fischer or that by Wassermann, the shape of a dianthraquinone molecule is not greatly different between the two isomeric forms. If this is the case, a molecule can be transformed from the one form to the other in the crystal without a drastic change in the crystal structure; accordingly, the energy required for this ought to be of the same order as that for a free molecule. On the other hand, Gruff and Kistiakowsky2) supposed that anthrone halves are perpendicular to each other in the high-energy form of the thermochromism, Matlow8) also showed later, by the molecular orbital treatment, that a triplet state is lower than the lowest singlet state for the conformation of the molecule mentioned above, and that the energy difference between this state and the ground state, in which anthrone halves are parallel to each other, is 3.3 kcal./mol., in good agreement with the observed energy difference between the two isomeric forms of the thermochromism. For the high-energy form, Kortüm and his collaborators also proposed a model in which anthrone halves are considerably twisted.3,6) If we assume models of this type, we must consider that the transformation of a dianthraquinone molecule to the high-energy form can not occur without producing quite a large distortion in the crystal lattice; consequently, the energy necessary for this transformation must be very large compared with that for a free molecule. This seems compatible with our experimental results, since we have actually observed that the formation of paramagnetic species is accompanied by the introduction of a marked disorder into the crystal lattice, and since the activation energy for the formation of the paramagnetic species in the crystal is large enough to assume such a process. In conclusion, we may suppose that the initial changes in the color and in the ESR absorption are due to the excitation of molecules to the state corresponding to the high-energy form of the thermochromism. In the solid state, however, once a molecule is transformed to such a state at an elevated temperature, it remains in that state even after the temperature is lowered, since a large activation energy is also required in the reverse process because of the necessary rearrangements of the neighboring molecules.

Naturally a molecule in the metastable triplet state is rather unstable, and can be expected to take part in the second process of the thermal change, a polymerization. The X-ray diffraction pattern of the heat-treated powder gives, however, little information on the structure of the polymerization product. The infrared absorption spectrum of the dark green solid of an amorphous structure prepared by 60 min. treatment at 270°C is shown in Fig. 6, together with the spectrum of the dianthraquinone powder. A sharp and strong absorption at 1650 cm^{-1} in the spectrum of dianthraquinone can be attributed to the C=O stretching vibration. Since this band changes little between the two spectra shown in Fig. 6, we can consider that the C=O group of dianthraquinone remains in the pyrolysis product. The absorption bands in the 1400—1600 cm^{-1} region, which are associated with the skeletal vibrations of the aromatic nucleus, are broadened a little. A remarkable change is found in the 650—950 cm^{-1} region, associated with the C–H bending vibrations.

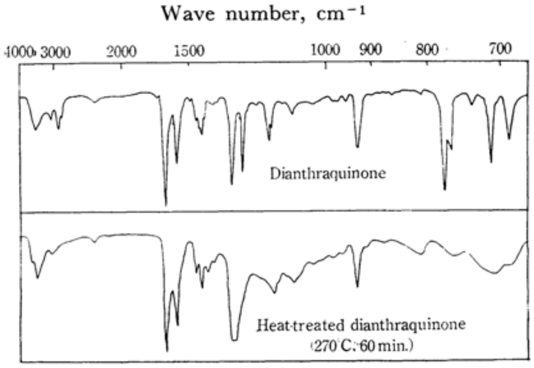

Fig. 6. The change in the infrared absorption spectrum of the dianthraquinone powder on heat-treatment.

These results seem to suggest that, in the polymerization product, the neighboring dianthraquinone molecules are connected by a bridge formed at the periphery of the anthrone halves, presumably at the expense of hydrogen atoms. Interestingly, the char obtained from the pyrolysis of dianthraquinone in the solid state is a non-graphitizing carbon. If the pyrolysis of dianthraquinone in the solid state proceeds in the manner suggested in the present paper, the orientations of aromatic nuclei may be expected to be quite random in the dianthraquinone-char. This might be what makes the char hard to be graphitized in heat treatment at high temperatures.

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