The Chemical Behavior of ^{64}Cu Recoil Atoms in the Mixed System of Copper Phthalocyanine and Metal-free Phthalocyanine

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In order to elucidate the effect of the crystal structure on the chemical behavior of ^{64}Cu recoil atoms in copper phthalocyanine, the author studied the mixed system of copper and metal-free phthalocyanine. It was found that the initial retention increased both in the mixed crystal and in the mixed-disk target. The addition of metal-free phthalocyanine sensitized the target to the thermal annealing reaction, and the rate of the reaction in the mixed crystal was faster than that in the unmixed crystal. The electron acceptor in the target was also found to increase the initial retention. The results were discussed in terms of the electrical properties of the target, which were changed by the change in the spatial arrangement of the molecules.

For the neutron-irradiated copper phthalocyanine, it has already been reported that the chemical consequence of ^{64}Cu recoil atoms depends greatly on the the crystal structure of the target.[1] The initial retention of the β-crystal yielded a higher value than that of the α-crystal. The results have been discussed in terms of the mobility of the recoil atom; *e.g.*, the channeling effect in the crystal depends upon the geometrical configuration of molecules. However, this does not seem the only possible explanation of the difference in the initial retentions in copper phthalocyanine. The intermolecular force and the physical properties of the crystal should inevitably change as the geometrical configuration of the molecules changes. In order to obtain further information leading to a solution of the problem, we studied the mixed system of copper and metal-free phthalocyanine.

Copper phthalocyanine, like other phthalocyanines, shows semiconductivity,[2–6] and the property of its crystal surface necessarily has a significant effect on the fate of the recoil atom. Metal-free phthalocyanine mixed with the target is expected to cause a change in the electrical properties of copper phthalocyanine.[7] It has also been reported[8] that magnesium phthalocyanine disks coated with a film of air-oxidized tetramethyl-*p*-phenylenediamine (TMPD) show a photovoltaic effect, while magnesium phthalocyanine alone exhibits no photovoltaic effect. The addition of chloranil to the surface of films of metal-free phthalocyanine has been found to produce charge carriers in the dark, to increase the quantum yield for the production of charge carriers in the light, and to increase the lifetime of the charge carrier.[9] Interest in the above facts has led to an investigation of the effect of the electron acceptor or the donor in the target.

Experimental

Materials. α-Copper phthalocyanine from Dainihon Ink and Chemicals was carefully purified by recrystallization from sulfuric acid. β-Copper phthalocyanine was obtained by suspending the α-crystal in benzene at 80°C for 2 hr. The α-crystal of metal-free phthalocyanine was prepared from cadmium phthalocyanine by demetallation in a sulfuric acid solution;[10] it was then sublimated *in vacuo* to obtain the β-crystal. The mixed crystal of copper and metal-free phthalocyanine (α-form) was prepared by dissolving appropriate quantities in concentrated sulfuric acid and by then pouring the solution into a large quantity of a mixture of ice and water.[7] The crystal modification of the target material was determined by means of a Philips Norelco X-ray diffractometer, using copper K_α radiation.

For the mixed-disk sample, appropriate quantities of copper and metal-free phthalocyanine were mixed in powder form and then pressed into disk ($\sim$50 mg/cm^2) under a pressure of 100 kg/cm^2. Chloranil from Dai-ichi Pure Chemicals was recrystallized from acetone. *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine dihydrochloride (TMPD), a product of a guaranteed reagent grade from Tokyo Kasei, was used without further purification.

Irradiation. The neutron irradiation of the target was performed at the temperature of dry ice (-78°C) for 10 sec in the nuclear reactor, JRR-2 (thermal neutron flux ϕ_{th}: 5.2×10^{13} n/cm^2/sec) or for 30 sec in the JRR-3 (ϕ_{th}: 2.0×10^{13} n/cm^2/sec). The γ-ray dose rates of the reactors were 1.2×10^8 R/hr and 1×10^8 R/hr respectively.

Chemical Separation and Radioactivity Measurements. The analytical method used here was virtually identical with that described previously.[1] The irradiated target was dissolved in cold sulfuric acid (<0°C), and then the solution was poured into a mixture of ice and water. The precipitate of copper phthalocyanine was then filtered out. The radioactivity of ^{64}Cu in both the precipitate and the filtrate was measured by means of a Baird Atomic single-channel γ-ray spectrometer connected to a NaI(Tl) crystal (well type, $1.75''\phi\times2''$).

Chloranil and the TMPD did not interfere with the course of the chemical separation.

Thermal Annealing. The irradiated mixed crystal was heated in a constant-boiling bath with an accuracy of ±0.5°C (<200°C) or in an electric furnace with the temperature

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[1] K. Yoshihara and H. Ebihara, *J. Chem. Phys.*, **45**, 896 (1966).

[2] D. D. Eley, *Nature*, **162**, 819 (1948).

[3] A. T. Vartanyan, *Zhur. Fiz. Khim.*, **22**, 769 (1948).

[4] C. J. Hoffman, *Quart. Rev.*, **18**, 113 (1964).

[5] F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds", Reinhold, New York (1963).

[6] A. B. P. Lever, "Advances in Inorganic Chemistry and Radiochemistry", Vol. 7, Academic Press, Inc., New York (1965) p. 27.

[7] E. A. Lucia and F. D. Verderame, *J. Chem. Phys.*, **48**, 2674 (1968).

[8] D. R. Kearns and M. Calvin, *ibid.*, **29**, 950 (1958).

[9] D. R. Kearns, G. Tollin, and M. Calvin, *ibid.*, **32**, 1020 (1960).

[10] H. Kudo and K. Yoshihara, *J. Inorg. Nucl. Chem.*, **32**, 2845 (1970).

controlled within ±1% (>200°C). No thermal decomposition in a gross amount was observed at any temperature.

Results

Prior to the study of the chemical behavior of the recoil atom in the mixed system of copper and metal-free phthalocyanine, the effect of pressing the crystal in the disk was examined. As is shown in Fig. 1, no discrepancy was observed between the untreated and the pressed targets. The initial retentions of both the pressed target and the untreated one were 5.5% for the α-crystal and 13.5% for the β-crystal.

Figure 2 shows the initial retention of the ^{64}Cu recoil atoms obtained in both the mixed crystal and the mixed disk of α-copper phthalocyanine as a function of the concentration of metal-free phthalocyanine in the target. Figure 3 shows the results for β-copper phthalocyanine. Although the shapes of the curves in these figures are not all the same, the initial retention increases in every case in which metal-free phthalocyanine is added. The mixture with the β-form of metal-free phthalocyanine shows a higher value than the mixture with the α-form of metal free phthalocyanine. This tendency is consistent with the finding that the initial retention for β-copper phthalocyanine is larger than that for the α-crystal.

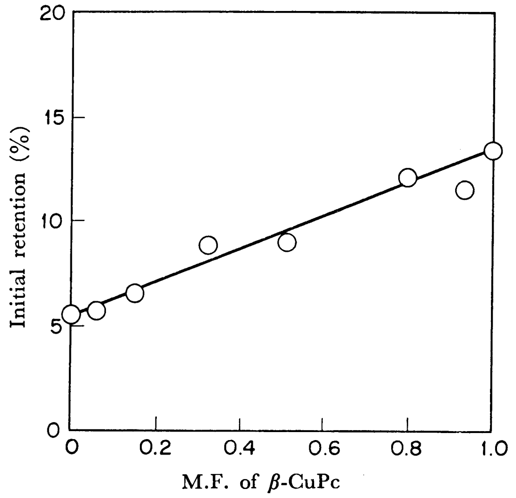

Fig. 1. The initial retention of ^{64}Cu recoil atoms in the mixed disk target of α- and β-copper phthalocyanine. (All samples were pressed under the pressure of 100 kg/cm^2.)

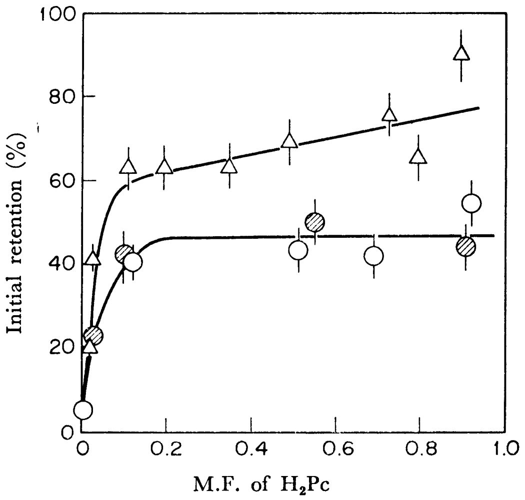

Fig. 2. The initial retention of ^{64}Cu recoil atoms in α-copper phthalocyanine (α-CuPc) mixed with metal-free phthalocyanine (H_2Pc): ○, the mixed crystal (α-form); ◍, the mixed disk with α-H_2Pc; △, the mixed disk with β-H_2Pc.

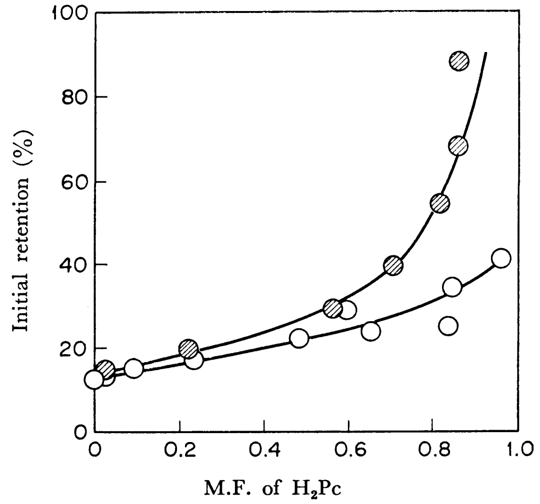

Fig. 3. The initial retention of ^{64}Cu recoil atoms in β-copper phthalocyanine mixed with metal-free phthalocyanine: ○, the mixed disk with α-H_2Pc; ◍, the mixed disk with β-H_2Pc.

A disk of α-copper phthalocyanine (100 mg/cm^2) was irradiated in close contact with a disk of metal-free phthalocyanine in the fashion illustrated in Fig. 4. A disk of α-copper phthalocyanine was attached to a disk (100 mg/cm^2) of metal-free phthalocyanine under pressure (Case (a)) or was pressed between two disks (50 mg/cm^2) of metal-free phthalocyanine (Case (b)). The initial retentions obtained were 16.8±2.5% and 20.8±3% respectively. These values are clearly higher than those obtained in the unmixed α-crystal.

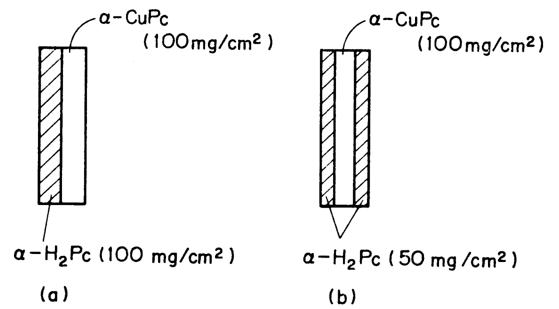

Fig. 4. The cross section of the contact disk target.

The thermal annealing process was studied for the mixed crystal. Figures 5 and 6 show the isothermal annealing curves of ^{64}Cu recoil atoms in the target which contain 0.04 M.F. and 0.53 M.F. of metal-free phthalocyanine respectively. In comparison

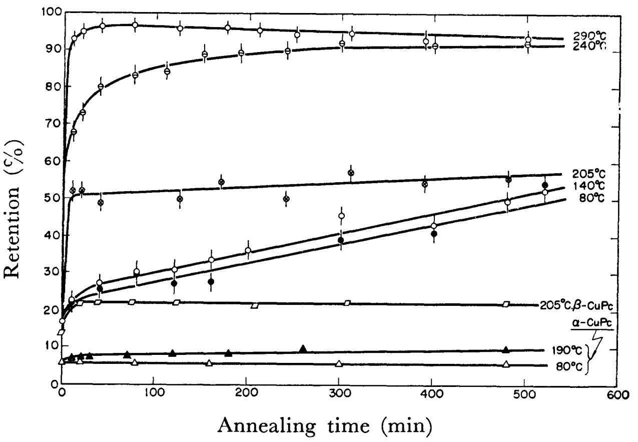

Fig. 5. The isothermal annealing curves for the mixed crystal which contains 0.04 M.F. of metal-free phthalocyanine.

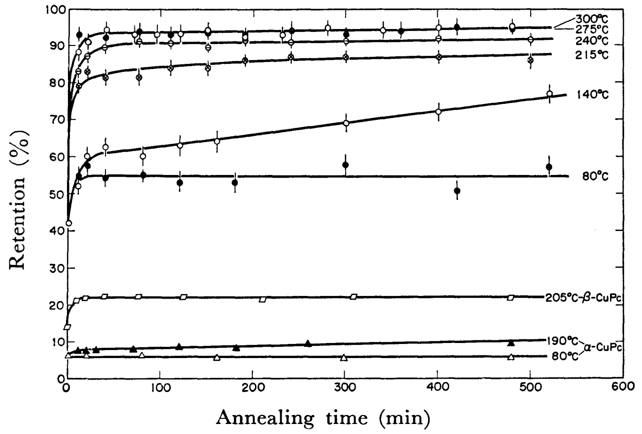

Fig. 6. The isothermal annealing curves for the mixed crystal which contains 0.53 M.F. of metal-free phtha o-cyanine.

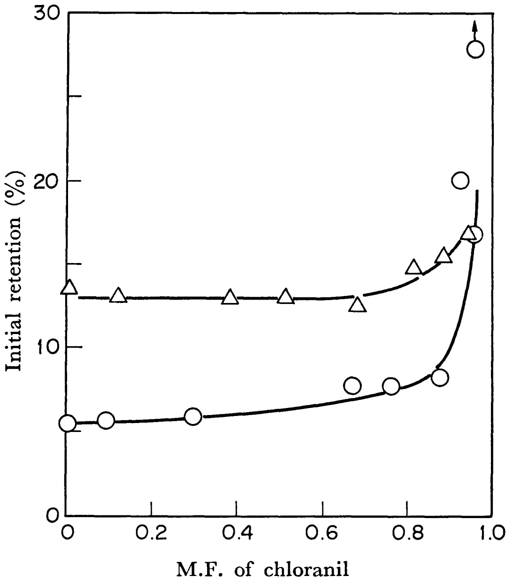

Fig. 7. The effect of chloranil added to copper phthalocyanine on the initial retention of ^{64}Cu recoil atoms. ○, α-crystal; △, β-crystal.

with the curves obtained for the unmixed α-crystal,[1,11] it is clear that, contrary to the case of the unmixed α-crystal, the reaction in the mixed crystal is completed below approximately 250°C. In contrast with the small annealable portion, ΔR, of Stage I (<200°C) in the unmixed crystal, the ΔR in the mixed crystal was very large, even below 200°C. As may be seen in Fig. 5, the retention at 80°C reached a higher value in the mixed crystal, whereas the thermal annealing reaction at the same temperature hardly proceeded at all in the unmixed α-crystal.

The addition of chloranil, as an electron acceptor, to the solid target of copper phthalocyanine was found to increase the initial retention of ^{64}Cu recoil atoms. The results are presented in Fig. 7. When the TMPD was added to the target as an electron donor, no effect on the initial retention was observed.

Discussion

The results presented in Fig. 2 are of great interest. The initial retention increases abruptly in the region of low concentrations of the added metal-free phthalycyanine, the value reaching a plateau in the region above 0.1 M.F. It can also be pointed out that the results obtained with the mixed-disk target of α-copper phthalocyanine with the α-crystal of metal-free phthalocyanine is virtually identical with that obtained in the mixed crystal.

Metal-free phthalocyanine should be distributed homogeneously in the lattice of the mixed crystal, so that it should be possible for the recoil atom to encounter the metal-free molecule in proportion to the concentration of metal-free phthalocyanine. If the recoil atom meets metal-free phthalocyanine in the course of its movement, it may enter the central position of the molecule, thus forming ^{64}Cu-phthalocyanine, since metal-free phthalocyanine has no central metal and two hydrogen atoms in the central space are easily replaced with divalent copper.[5,6] This should lead to an increase in the initial retention.

In the case of the mixed disk target, however, metal-free phthalocyanine may be expected to be mixed rather heterogeneously with copper phthalocyanine. The size of each particle is estimated to be of the order 0.1 μ. Considering the maximum recoil range of ^{64}Cu recoil atoms produced by the ^{63}Cu(n,γ)^{64}Cu reaction in copper phthalocyanine (the order of some tens of Å), it is less probable that the recoil atom interacts directly with metal-free phthalocyanine. Nevertheless, similar results were obtained in the mixed crystal and in the mixed-disk target. From these results, it seems reasonable that metal-free phthalocyanine added to the target indirectly affects the course of the determination of the chemical fate of the recoil atom. The indirect contribution of metal-free phthalocyanine may be supported further by the fact that the initial retention increases when the disk of α-copper phthalocyanine is irradiated in contact with the disk of metal-free phthalocyanine. On the basis of these data, it is possible to say that

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[11] H. Kudo, This Bulletin, **45**, 389 (1972).

the chemical consequence of the recoil atom strongly depends either on the physical properties of the crystal or on the reaction taking place in the neighborhood of the crystal surface.

As is shown in Figs. 5 and 6, the addition of metal-free phthalocyanine sensitizes the target to the thermal annealing reaction; the annealable portion, ΔR, of Stage I increases remarkably. This may be explained in the same manner as the increase of the initial retention, by assuming that the Stage-I annealing process reflects the initial recoil reaction.[1,12] It is also instructive to note that the rate of the thermal annealing reaction in the mixed crystal, especially at 205°C in the target containing 0.04 M.F. of metal-free phthalocyanine, is faster than that of the unmixed α-crystal. The faster rate of the reaction may be attrubuted to the reaction of the recoil atom at the crystal surface.

Thus, the property of the crystal surface of the phthalocyanine complex may be supposed to play a significant role in determining the chemical behavior of the recoil atom. This is also supported by the results presented in Fig. 7. The addition of chloranil as an electron acceptor to the copper phthalocyanine disk was found to increase the initial retention, although the TMPD, an electron donor, did not appear to affect the initial retention. The results indicate that an electron transfer from copper phthalocyanine to chloranil may have a strong effect on the behavior of the recoil atom.

The conductivity of the α-crystal of metal-free phthalocyanine has been reported[13,14] to be approximately ten times, in special cases more nearly 10^5 times, greater than that of the β-crystal. The values of the energy intervals, based on the band-theory model, of the β-crystals of several metal phthalocyanines lie between 1.5 and 1.7 eV.[15] A much lower value, 0.5 eV, has been reported for the energy interval of the α-crystal.[14] The charge transport in the complex has been explained by an out-of-plane interaction of π-electrons of the conjugated ring structure of the phthalocyanine with the antibonding orbitals of nitrogen atoms in the molecules above and below it.[16] Since the interaction takes place at the distance of the nearest approach of adjacent molecules, the molecular dimensions and the arrangement are important factors in determining the electrical conductivity in the solid. That is, the change in the spatial arrangement of molecules causes a change in the electrical properties of the target and may affect the chemical behavior of the recoil atom in the target.

In the present study of the chemical behavior of ^{64}Cu recoil atoms in the mixed system of copper and metal-free phthalocyanine, the electrical property of the target was suggested to be one of the most significant factors, although it is difficult to conclude at present what parameter of the electrical properties plays a role in determining the chemical fate of the recoil atom. As was mentioned in the last paragraph, the electrical property depends on the spatial arrangement of the molecules. This may lead to an understanding of the crystal-structure dependence of the initial retention in copper phthalocyanine. That is, the channeling effect and also the electrical property of the target might be factors which determine the chemical behavior of the recoil atom.

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12) M. H. Yang, *Radiochim. Acta*, **12**, 167 (1969).

13) D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, **51**, 1529 (1955).

14) K, Wihksne and A. E. Newkirk, *J. Chem. Phys.*, **34**, 2184 (1961).

15) D. D. Eley, *Research*, **12**, 293 (1959).

16) G. H. Heilmeir and S. E. Harrison, *Phys. Rev.*, **132**, 2010 (1963).