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THE PARTICIPATION OF LIGHT IN THE FORMATION OF PHTHALOCYANINE

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It was found that roomlight accelerates the formation of phthalocyanine in the reaction of phthalonitrile with sodium alkoxide at elevated temperatures. Moreover, UV irradiation gave phthalocyanine even at room temperature where no formation of phthalocyanine was observed without light.

There are several methods for the preparation of phthalocyanine.[1-3] The general method for preparing phthalocyanine is to heat phthalonitrile with sodium alkoxide in alcohol. In a study of the above thermal reaction, we made remakable observation that roomlight affected the formation of phthalocyanine. Moreover, it was found that phthalocyanine was also obtained when the reaction system was irradiated with UV light at room temperature.

The procedure was as follows. After sodium metal (0.115 g, 5 mmol) was dissolved in 125 ml of alcohol, phthalonitrile (1.28 g, 10 mmol) was added to the solution. The preparation in the dark or under roomlight was carried out by heating the solution under reflux for 48 h under nitrogen atmosphere. The photochemical preparation was carried out either at room temperature or at 70 °C by irradiating internally with UV light for 48 h under nitrogen atmosphere. The precipitated blue product, phthalocyanine, was collected by filtration, washed with hot ethyl alcohol and dried. The product was identified by infrared spectra.

The yields of phthalocyanine under various conditions are shown in Table 1. When the reaction mixture was allowed to stand for 48 h with magnetic stirring at room temperature in the dark or under roomlight, the formation of phthalocyanine was not observed at all. At elevated temperatures, the yield of phthalocyanine

Table 1. Formation of Phthalocyanine from Phthalonitrile and Sodium Alkoxide under Various Conditions

Alcohol	Phthalocyanine Yield (%)					
	Room Temperature			Reflux Temperature		70 °C
	Dark	Roomlight[a]	hν[b]	Dark	Roomlight[a]	hν[b]
CH_3OH	0	0	2.9	0	0	29.3
C_2H_5OH	0	0	3.1	trace	0.2	17.4
n-C_3H_7OH	0	0	15.7	3.1	6.6	19.8
i-C_3H_7OH	0	0	3.6	0	0	18.2
n-C_4H_9OH	0	0	16.1	4.4	14.9	24.7
i-C_4H_9OH	0	0	12.5	12.5	23.6	22.8
s-C_4H_9OH	0	0	0	14.0	15.3	9.5
t-C_4H_9OH	0	0	0	0	0	0
n-$C_5H_{11}OH$	0	0	12.7	11.3	35.3	35.3
i-$C_5H_{11}OH$	0	0	15.3	22.4	47.4	40.3

a) under room-fluorescent lamp

b) 100 W high pressure mercury lamp with a Pyrex filter

under roomlight was better than that in the dark. These results show that the light participates in the formation of phthalocyanine.

Table 1 shows that the formation of phthalocyanine occurred by UV irradiation even at room temperature. When the UV irradiation was carried out at 70 °C, the yields of phthalocyanine increased. In isopropyl alcohol, the thermal reaction did not give phthalocyanine while the UV irradiation did.

After the solution had been pre-irradiated with UV light at room temperature, the mixture was refluxed for 45 h in the dark. The yield of phthalocyanine increased in proportion to UV pre-irradiation time (Fig. 1). However, when a solution which had been heated for 45 h in the dark was exposed to UV light for 48 h, the formation of phthalocyanine was not observed at all. This indicates that the irradiation of the reaction mixture was effective at the initial stage of the reaction. Phthalonitrile showed transient UV absorptions at 680 nm and around 500 nm after UV irradiation at room temperature, but showed another absorption at 407 nm by heating

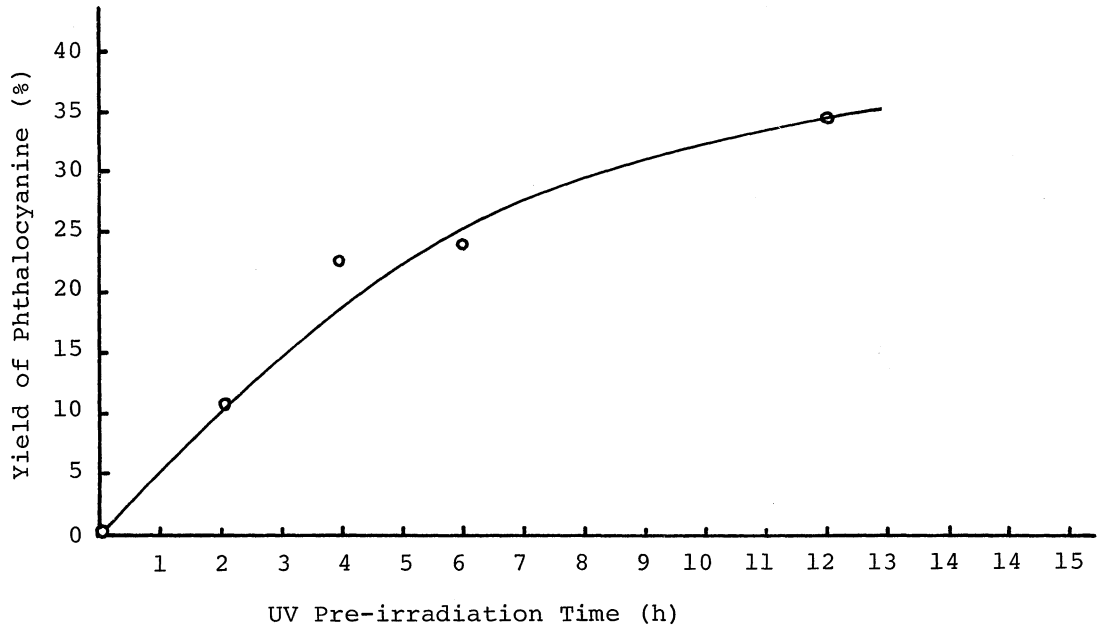

Fig.1. Relation between The Yield of Phthalocyanine and UV Pre-irradiation Time
Conditions; phthalonitrile (10 mmol) and sodium metal (5 mmol) in methyl alcohol (125 ml); reflux time: 45 h

Table 2. Effect of Oxygen and Benzene on The Formation of Phthalocyanine by UV Irradiation[a)]

Temperature (°C)	Atmosphere	Additive	Phthalocyanine Yield (%)
25	air	—	0
25	N_2	—	2.9
25	N_2	Benzene[b)]	11.2
70	air	—	16.0
70	N_2	—	29.3
70	N_2	Benzene[b)]	34.5

a) phthalonitrile (10 mmol) and sodium metal (5 mmol) in methyl alcohol (125 ml)

b) 25 ml of methyl alcohol and 100 ml of benzene

in the dark. These absorptions could be ascribed to some intermediates, but they have not yet been identified.

The yield of phthalocyanine in the photochemical reaction was decreased by air to a greater extent than that in the thermal reaction. As Table 2 shows, the formation of phthalocyanine was inhibited by air at room temperature, the yield of phthalocyanine at 70 °C in the presence of air being about 1/2 of that in its absence. When UV irradiation was done in the presence of benzene under nitrogen atmosphere, the yield of phthalocyanine was better than that in the absence of benzene.

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