Syntheses of Chlorinated Copper Phthalocyanines from Chlorophthalic Anhydrides

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As a method of synthesis of copper phthalocyanine, the urea-method[1] resorting to the condensation of phthalic anhydride, urea and copper salts prevails. Chlorinated copper phthalocyanines can be obtained by the use of chlorophthalic anhydrides instead of phthalic anhydride. However, since chlorinated copper phthalocyanines are manufactured by chlorinating copper phthalocyanine, little work has been done upon the syntheses of them from chlorophthalic anhydrides.

The author carried out the syntheses of chlorinated copper phthalocyanines by the urea-method, using chlorophthalic anhydrides instead of phthalic anhydride and studied the effect given by the chlorine atoms of starting materials.

Experimental

Materials.—*Phthalic anhydride* (I).—Commercial phthalic anhydride was used with further purification (m. p. 130~131°C).

Monochlorophthalic anhydrides. — By the improved V. Villiger's method[2,3], phthalic anhydride was chlorinated with chlorine gas at 50~55°C in an iron closed vessel, using oleum as solvent and iodine as catalyst. From the mixture of monochlorophthalic anhydrides thus prepared, were separated 3-monochlorophthalic anhydride (II), m. p. 121~122°C (reported m. p. 122°C[4]) (*Anal.* Found: Cl, 19.47%) and 4-monochlorophthalic anhydride (III), m. p. 97~98°C (reported m. p. 98°C[4]) (*Anal.* Found: Cl, 19.44%) by repeating recrystallization with toluene-ethanol (1 : 1) solvent.

Dichlorophthalic anhydrides. — From the mixture of dichlorophthalic anhydrides prepared by the same procedure as above, were separated 3,4-dichlorophthalic anhydride (IV), m. p. 120~121°C (reported m. p. 120~121°C[4]) (*Anal.* Found: Cl, 32.68%), 3,6-dichlorophthalic anhydride (V), m. p. 190~191°C, (reported m. p. 190~191°C[4]) (*Anal.* Found: Cl, 32.71%) and 4,5-dichlorophthalic anhydride (VI), m. p. 185.5~186.5°C (reported m. p. 185~187°C[4]) (*Anal.* Found: Cl, 32.66%) with toluene-ethanol (1:1) solvent.

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[1] U. S. Pat. 2,197,458 (1940).

[2] V. Villiger, *Ber.*, **42**, 3538 (1909).

[3] M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 110 (1959). (Presented at the Autumnal Joint Meeting of Chemical Society of Japan with other Societies, Tokyo, 1957).

[4] V. Villiger, *Ber.*, **42**, 3532 (1909).

Trichlorophthalic anhydrides.— From the mixture of trichlorophthalic anhydrides prepared by the same procedure as above, were separated 3, 4, 6-trichlorophthalic anhydride (VII), m. p. 147.5～148.5°C (reported m. p. 148°C[5]) (*Anal.* Found: Cl, 42.19%) and 3, 4, 5-trichlorophthalic anhydride (VIII), m. p. 155.5～156.5°C (reported m. p. 157°C[6]) (*Anal.* Found: Cl, 42.20%) with toluene-ethanol (1:1) solvent.

Tetrachlorophthalic anhydride (IX). — By N. Juvalta's method[7], phthalic anhydride was chlorinated with chlorine gas at 50～60°C and thereafter 200°C in oleum, using iodine as catalyst, and the product was recrystallized with toluene-ethanol (1:1) solvent; m. p. 255～256.5°C (reported m. p. 255～256.5°C[8]) (*Anal.* Found: Cl, 49.22%).

Methods.—Into a three-necked flask of 300 cc. capacity equipped with a stirrer, a thermometer and a reflux condenser were placed 4 : 20 : 1 mol. ratio mixture of phthalic anhydride or its chlorinated derivatives, urea and cuprous chloride as indicated in Table I, and 150 g. of trichlorobenzene used as solvent.

The mixture was stirred at room temperature for 30 min., and then heated to 175°C for 1 hr. at a uniform rate and finally at 175～180°C for 3 hr. After the reaction was complete, trichlorobenzene was removed by steam distillation and the product was heated with 5% hydrochloric acid and then with 2% caustic soda, filtered, washed with water and ethanol and dried at 95～100°C.

In the case of tetrachlorophthalic anhydride, the reaction was conducted with the addition of ammonium molybdate[9], boric acid[1], zirconium tetrachloride[10] and titanium tetrachloride[10] as catalysts of condensation.

Results and Discussion

Results of condensation of phthalic anhydride or its chlorinated derivatives with urea and cuprous chloride are given in Table I.

Phthalic anhydride easily reacts with urea and cuprous chloride and forms copper phthalocyanine. However, when the chlorine content of phthalic anhydride increases, the yield of the product decreases.

The yields obtained in Experiments 3, 6 and 8 are all larger than those obtained in Experiments 2, 5 and 7. Experiment 4 shows the yield between those obtained in Experiments 5 and 6. It is recognized from the above experiments that chlorinated copper phthalocyanines are formed from chlorophthalic anhydrides more easily when chlorine atoms are in 4, 5-positions of phthalic anhydride than when they are in its 3, 6-positions.

Although copper hexadecachlorophthalocyanine should be obtained in Experiment 9, the chlorine content of the product coincides with that of copper dodecachlorophthalocyanine. The author further studied this matter as follows.

Ammonium molybdate, boric acid, zirconium tetrachloride and titanium tetrachloride are used as catalysts to increase the yield of phthalocyanine formed in

TABLE I. CONDENSATION OF PHTHALIC ANHYDRIDE OR ITS CHLORINATED DERIVATIVES WITH UREA AND CUPROUS CHLORIDE

				Product				
Expt.	Starting material	Urea	Cuprous chloride	Wt.	Yield	Cl (%)		
						Found	Calcd.	
	(g.)	(g.)	(g.)	(g.)	(%)			
1	I, 10.0	19.3	1.7	A, 8.6	89	0.09	0	($C_{32}H_{16}N_8Cu$)
2	II, 10.0	13.7	1.4	B, 7.4	76	19.76	19.87	($C_{32}H_{12}N_8Cl_4Cu$)
3	III, 10.0	13.7	1.4	C, 8.3	85	19.80	〃	〃
4	IV, 10.0	11.6	1.2	D, 7.3	75	33.19	33.24	($C_{32}H_8N_8Cl_8Cu$)
5	V, 10.0	11.6	1.2	E, 6.9	70	33.22	〃	〃
6	VI, 10.0	11.6	1.2	F, 7.8	80	33.18	〃	〃
7	VII, 10.0	9.9	1.0	G, 5.9	60	42.98	43.02	($C_{32}H_4N_8Cl_{12}Cu$)
8	VIII, 10.0	9.9	1.0	H, 6.8	69	43.01	〃	〃
9	IX, 10.0	8.8	0.9	I, 4.1	42	43.04	50.34	($C_{32}N_8Cl_{16}Cu$)

A, Copper phthalocyanine.
B, Copper tetra-(3)-chlorophthalocyanine.
C, Copper tetra-(4)-chlorophthalocyanine.
D, Copper octa-(3, 4)-chlorophthalocyanine.
E, Copper octa-(3, 6)-chlorophthalocyanine.
F, Copper octa-(4, 5)-chlorophthalocyanine.
G, Copper dodeca-(3, 4, 6)-chlorophthalocyanine.
H, Copper dodeca-(3, 4, 5)-chlorophthalocyanine.
I, To be discussed later.

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[5] C. Graebe and S. Rostowzew, ibid., **34**, 2108 (1901).

[6] Ad. Claus and H. Kautz, ibid., 18, 1370 (1885).

[7] D. R. Pat. 50,177 (1889).

[8] D. S. Pratt and G. A. Perkins, *J. Am. Chem. Soc.*, **40**, 204 (1918).

[9] U. S. Pat. 2,214,477 (1940).

[10] U. S. Pat. 2,549,842 (1951).

TABLE II. CONDENSATION OF TETRACHLOROPHTHALIC ANHYDRIDE WITH UREA AND CUPROUS CHLORIDE

Expt.	IX	Urea	Cuprous chloride	Catalyst	Product		
	(g.)	(g.)	(g.)	(g.)	Wt. (g.)	Yield (%)	Cl (%)
10	10.0	8.8	0.9	A, 0.5	4.6	47	43.25
11	10.0	8.8	0.9	B, 0.5	4.9	50	43.51
12	10.0	8.8	0.9	C, 0.5	5.9	60	45.95
13	10.0	8.8	0.9	D, 0.5	5.4	55	44.73

A, Ammonium molybdate. B, Boric acid.
C, Zirconium tetrachloride. D, Titanium tetrachloride.

urea-method. Using these compounds as catalysts and under the reaction conditions in Table I, IX was condensed with urea and cuprous chloride. The results are given in Table II.

In Table II, the yield in Experiment 12 is the largest, but it is only 60%. The larger the yield, the larger the chlorine content is. However, all the chlorine contents in Table II are smaller than that of copper hexadecachlorophthalocyanine and close to that of copper dodecachlorophthalocyanine.

As it was considered that dechlorination reaction might possibly occur in the formation of phthalocyanine, the product obtained in Experiment 9 (Table I) was examined. Based on the method in Ref. 11, 3 g. of the product was decomposed by oxidation with ceric sulfate, which gave 2.0 g. of 3,4,5-trichlorophthalic anhydride, m. p. 156~157°C (reported m. p. 157°C[6)]) (*Anal.* Found: Cl, 42.17%). It was evident from the above experiments that the chlorine atom at 6-position of IX separated and condensed with urea and cuprous chloride.

Summary

Syntheses of chlorinated copper phthalocyanines from various chlorophthalic anhydrides were conducted. Formation of phthalocyanine depends upon the contents and positions of chlorine atoms of chlorophthalic anhydrides.

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11) R. P. Linstead el al., *J. Chem. Soc.*, **1939**, 1823.