coupling produced by a common benzene linkage results in a repression of the absorption band.

Summary

Measurements of the absorption spectra of a number of disazo dyes in various solvents have been made and their correlation with the chemical constitution of the dyes has been discussed.

COLUMBUS, OHIO RECEIVED OCTOBER 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Adsorption at Crystal–Solution Interfaces. XII. A Study of the Adsorption of Isomeric Dyes by Crystals of Cupric Acetate during their Growth from Solution*

BY WESLEY G. FRANCE AND KATHRYN M. WOLFE

This paper like the preceding two, X and XI,[1] of this series on the adsorption at crystal–solution interfaces is concerned primarily with the effect of certain polar groups in the foreign molecules. In those studies it was found that the dyes containing sterically hindered groups were in general not adsorbed by the crystals. It was thought desirable in order to obtain further information on this steric adsorption effect to extend this investigation to include a crystal belonging to a system as yet not studied. Cupric acetate monohydrate was selected. At 30° it crystallizes in dark green rhombohedra. It belongs to the holohedral class of the monoclinic system. No data appear to have been published concerning the unit cell of this crystal. Few colored crystals have previously been used in similar investigations. However, Buckley[2] in studying the growth and variation of the crystal of pure potassium chlorate used certain permanganate and chromate salts as impurity. These were used as impurity rather than as the substance undergoing modification.

The same dyes were employed in this study as by Rigterink and France[1] and by France and Wolfe[1] in their investigations of potassium sulfate, sodium nitrate, sodium bromate and sodium chlorate. These dyes are members of two series of isomers prepared by coupling aniline and the ortho-, meta- and para-sulfonated anilines by the usual diazotization method with a series of mono- and di-sulfonic acid derivatives of α- and β-naphthols and α- and β-naphthylamines. The abbreviations in the tables are derived from the intermediates used in their preparation. These intermediates are: aniline (A), ortho-sulfonated aniline (O), meta-sulfonated aniline (M), para-sulfonated aniline (P), α-naphthol (α-OH), β-naphthol (β-OH), α-naphthylamine (α-NH_2) and β-naphthylamine (β-NH_2). The numbers given in the tables after the abbreviations refer to the positions of the —SO_3Na groups attached to the naphthalene rings.

Experimental

The solutions in which the crystals were grown were made by heating enough dye with the saturated solution of the salt so that upon subsequent cooling in the constant temperature room for twenty-four hours at $30 \pm 0.2°$ some of the dye precipitated. The solutions were then filtered into 20-cc. vials, two for each dye used and single seed crystals were suspended in the solutions by copper wire attached by de Khotinsky cement. The crystals were allowed to grow for ten days.

Results.—The results are summarized in Tables I, II, III and IV. All of the eighty-six dyes recorded in the paper by Rigterink and France[1] were used. However, only those which modified the cupric acetate are recorded in the tables. The types referred to in the tables are as follows.

Type 1.—The growth rate between a pair of parallel orthodome faces was retarded, thus developing this pair of faces shown in Fig. 1.

Type 2.—A stair-step-like formation of planes was formed parallel to the faces of the crystal.

Of the forty-two dyes which modified the crystal habit of cupric acetate forming type 1 there were

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* Presented to the Colloid Division of the American Chemical Society, Detroit Meeting, September, 1940.

[1] McBurney and France, THIS JOURNAL, **46**, 540 (1924); Eckert and France, *J. Am. Ceram. Soc.*, **10**, 579 (1927); Keenen and France, *ibid.*, **10**, 821 (1927); Bennett and France, *ibid.*, **11**, 571 (1928); France, *Colloid Symposium Annual*, **7**, 59 (1930); Lash and France, *J. Phys. Chem.*, **34**, 724 (1930); Foote, Blake and France, *ibid.*, **34**, 2236 (1930); Weinland and France, *ibid.*, **36**, 2832 (1932); Starr, Master's Thesis, O. S. U., 1933; Paine and France, *J. Phys. Chem.*, **39**, 425–429 (1935); Davis and France, *ibid.*, **40**, 81–87 (1936); Rigterink and France, X, *ibid.*, **42**, 1079 (1938); Wolfe and France, XI, a paper presented at the Colloid Division of the American Chemical Society Meeting, Cincinnati, Ohio, April 8–12, 1940.

[2] Buckley, *Z. Krist.*, **82**, 31–36, 37–46, 47–49 (1932).

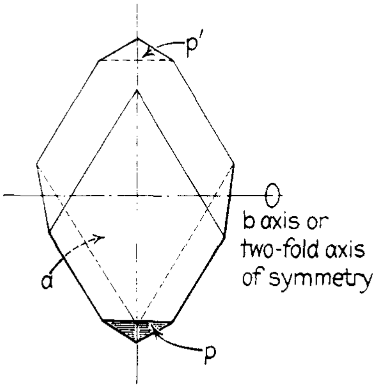


Fig. 1.—Cupric acetate crystal.

nine pairs. Each one of a pair has exactly the same structure except that the acid dye contains an —OH group in the same position in which the basic dye possesses an —NH_2 group. In six of these dyes the —OH or the —NH_2 group is in the alpha position on the naphthalene ring; in six there is a sulfonic acid group in the meta position on the benzene ring; in three there is a sulfonic acid group in position 3 on the naphthalene ring; in two a sulfonic acid group in position 5; in one a sulfonic acid group in position 6 and in one there is a sulfonic acid group in position 7. There are no pairs of acid *versus* basic dyes which direct the formation of stair-step-like planes but there are two pairs of acid dyes and one pair of basic dyes which are comparable. These are: A α OH-5, O α OH-5, A β OH-6:8, O β OH-6:8, A α NH_2-8, O α NH_2-8. It is to be noted that these three pairs of dyes differ only in that one dye of a pair contains an —SO_3Na group in the ortho position on the benzene ring while the other has no —SO_3Na group on the benzene ring. The acid dyes which have the same structure as the basic dyes

TABLE I

SUMMARY OF EFFECT OF SOLUBLE ACID DYES ON CUPRIC ACETATE

Dye formula	Modification, type	Type of nucleus
M α OH	1	A
A α OH-3	1	B
M α OH-3	1	B
P α OH-3	1	B
O α OH-3:8*x*	1	B
A α OH-4	1	B
M α OH-4	1	B
P α OH-4	2	B
A α OH-5	2	B
O α OH-5	2	B
M α OH-5	1	B
P α OH-5	1	B
O β OH	1	A
M β OH	1	A
A β OH-3:6*x*	1	A
O β OH-3:6*x*	1	A
M β OH-3:6*x*	1	A
P β OH-3:6*x*	1	A
O β OH-6	1	A
M β OH-6	1	A
P β OH-6	1	A
A β OH-6:8*x*	2	A
O β OH-6:8*x*	2	A
M β OH-6:8*x*	1	A
O β OH-7	1	A
P β OH-7	1	A

TABLE II

SUMMARY OF EFFECT OF SOLUBLE BASIC DYES ON CUPRIC ACETATE

Dye formula	Modification, type	Type of nucleus
O α NH_2	1	A
M α NH_2	1 and twinning	A
O α NH_2-2*x*	1 and twinning	A
M α NH_2-2*x*	1	A
A α NH_2-3	1	B
O α NH_2-3	1	B
M α NH_2-3	1	B
P α NH_2-3	1	B
O α NH_2-4	1	B
P α NH_2-4	1	B
M α NH_2-5	1	B
P α NH_2-5	1	B
M α NH_2-6*x*	1	A
O α NH_2-7*x*	2	A
P α NH_2-7*x*	1	A
A α NH_2-8*x*	2	A
O α NH_2-8*x*	2	A
P α NH_2-8*x*	1	A
M β NH_2	1	A
P β NH_2	1	A
M β NH_2-6	1	A
A β NH_2-7	1	A
M β NH_2-7	1	A
P β NH_2-7	1	A

TABLE III

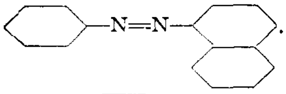
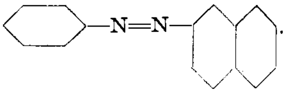
PAIRS OF DYES WHICH CAUSED GROWTH TO BE RETARDED BETWEEN A PARALLEL PAIR OF ORTHODOME FACES

Acid dyes	Basic dyes
M α OH	M α NH_2
A α OH-3	A α NH_2-3
M α OH-3	M α NH_2-3
P α OH-3	P α NH_2-3
M α OH-5	M α NH_2-5
P α OH-5	P α NH_2-5
M β OH	M β NH_2
M β OH-6	M β NH_2-6
P β OH-7	P β NH_2-7

TABLE IV

PAIRS OF DYES WHICH DIRECT THE FORMATION OF STAIR-STEP-LIKE PLANES

A α OH-5	A β OH-6:8	A α NH_2-8
O α OH-5	O β OH-6:8	O α NH_2-8

marked with an *x* in the tables and likewise the basic dyes which have the same structure as the acid dyes marked with an *x* were not available and therefore were not used in this study. Omitting the dyes marked with an *x* there are only thirty-one different formulas for dyes recorded which caused retardation of growth between a parallel pair of orthodome faces. Eighteen of these formulas represent nine pairs of dyes, one acid and one basic per pair which changed the crystal habit to type 1. Twenty-six of the forty-two dyes which changed the habit to type 1 possess nucleus A, . Sixteen possess nucleus B, . Five of the eight dyes which changed the habit in such a manner that stair-step-like planes were formed also possess nucleus A.

Acknowledgment.—The authors acknowledge their appreciation for suggestions offered by Dr. P. M. Harris, Department of Chemistry, Ohio State University.

Conclusions

The M and P dyes predominate in the formation of orthodome faces on cupric acetate while the A and O dyes predominate in the stair-step formation.

2. The majority of the dyes adsorbed possess nucleus A. This is in accordance with Rigterink and France's data[1] and a previous report by France and Wolfe.[1]

3. Nine pairs of dyes differing only in an —NH_2 group replacing an —OH group on the naphthalene ring have the same effect on the crystal habit of cupric acetate. This differs appreciably from the results obtained by Rigterink and France[1] in their studies of potassium sulfate.

4. Judging from the manner in which these dyes were adsorbed by crystals of known crystal lattice, one is led to conclude that the orthodome faces of cupric acetate are populated by alternate layers of positive and negative ions. It is also very probable that the carbon atoms of the acetate groups lie along the two-fold axis of symmetry. The lack of hardness and the boiling point of cupric acetate suggest the possibility of a layer lattice.

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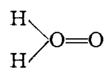
The Crystal Structure of the Urea–Hydrogen Peroxide Addition Compound $CO(NH_2)_2 \cdot H_2O_2$

BY CHIA-SI LU, E. W. HUGHES AND PAUL A. GIGUÈRE

The molecular structure of hydrogen peroxide has been the subject of numerous investigations[1] during the last few years. No definite choice between the two proposed structures I and II[1,2] could be made from chemical evidence alone. Linton and Maass[3] favored structure II on the

I. HOOH II 

$$H_2>O=O$$

basis of their determination of the dipole moments of hydrogen peroxide in solutions. Theilacker,[4] on the other hand, pointed out that the same dipole moment and parachor data could be equally well accounted for by structure I, if the OH groups were assumed to be free to rotate around the O–O bond. In 1934 Penney and Sutherland[5] made a quantum-mechanical calculation for this molecule by the method of electron pairs, and showed that the energy dependence on the azimuthal angle ϕ between the planes of the two OH groups is more dominantly governed by the interaction of the non-axis-symmetrical electronic distributions around the two oxygen atoms than by the interaction between the two hydrogen atoms. They found that structure III in which ϕ and θ (= $\angle$H–O–O) are both about 100° would be about 10,000 cal./mole more stable than either the *cis* or the *trans* configuration ($\phi = 0°$ or 180°). This structure gives a value of the dipole moment in good agreement with that determined

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[1] For a good summary, see W. Machu, "Das Wasserstoffperoxyd und die Perverbindungen," Verlag Julius Springer, Berlin, 1937.

[2] See J. W. Mellor, "Treatise on Inorganic Chemistry," Longmans, London, 1922.

[3] E. P. Linton and O. Maass, *Can. J. Research*, **7**, 81 (1932).

[4] W. Theilacker, *Z. physik. Chem.*, **B20**, 142 (1933).

[5] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).