can be separated by crystallization from 95% alcohol in which the glycereins are soluble. These compounds have been found to be pyronine dyes.

4. A close study of the fluorescence of the benzeins and the naphthaleins has shown that there is no appreciable difference in their fluorescence in dil. alkaline solutions, but the naphthaleins dye a deeper shade than the benzeins. The glycereins with aliphatic groups in place of the phenyl residues of the benzeins show fluorescence similar to that of the benzeins but dye weaker shades, whereas the acroleins have a faint green fluorescence and have practically no tinctorial properties. The pyrogallol and the gallic acid compounds dye brown to blackish-brown shades; the former have no fluorescence in any solvent, whereas the latter show a strong green fluorescence in concd. sulfuric acid.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

PREPARATION AND PROPERTIES OF DICHLORO-ACETIC ACID

BY HOWARD WATERS DOUGHTY AND ARTHUR PROCTOR BLACK

RECEIVED OCTOBER 21, 1924 PUBLISHED APRIL 4, 1925

Dichloro-acetic acid has been prepared in a variety of ways, of which the following are the most important.

Maumené[1] obtained it by direct chlorination of monochloro-acetic acid. Müller[2] by chlorination of acetic acid in presence of iodine. Wallach[3] by the action of potassium cyanide on chloral in aqueous solution. Brand[4] by electrolytic reduction of trichloro-acetic acid. In 1922 Doughty and Freeman[5] found that dichloro-acetic acid is formed when copper powder and trichloro-acetic acid react in benzene or aqueous solution and that tetrachloro-succinic acid is also formed in small quantity when the reaction takes place in ether or without any solvent. They also prepared ethyl tetrachloro-succinate from ethyl trichloro-acetate and copper powder.

This investigation was undertaken to determine the conditions for maximum yield of dichloro-acetic acid by the method of Doughty and Freeman, and also to determine some of the physical constants of this acid, both as criteria of the purity of the acid thus obtained and on account of the fact that considerable discrepancy exists in the boiling point of the acid as recorded by various observers.

It was soon found that the reaction requires more copper than was used by Doughty and Freeman. They used three molecular equivalents of copper to two of trichloro-acetic acid, and when this proportion is used trichloro-acetic acid is always found in the product; but when two equiva-

[1] Maumené, *Compt. rend.*, **59**, 84 (1864); *Ann.*, **133**, 154 (1865).

[2] Müller, *Ann.*, **133**, 159 (1865).

[3] Wallach, *Ann.*, **173**, 295 (1874).

[4] Brand, Ger. pat. 246,661 (1911).

[5] Doughty and Freeman, THIS JOURNAL, **44**, 636 (1922).

lents of copper are used to one of trichloro-acetic acid, the reaction is complete. It is necessary to stir continuously and to add the copper in small quantities during the reaction, as otherwise it becomes coated with cuprous chloride, protecting it from further action. When the reaction takes place in boiling benzene, gas is evolved, about two liters being obtained in one experiment in which 100 g. of trichloro-acetic acid was used. This gas contained by analysis, 77% of carbon monoxide and 15% of carbon dioxide. At lower temperatures no gas is formed.

Effect of Solvent. Anticatalytic Effect of Carbon Tetrachloride.—The reaction between trichloro-acetic acid and copper is evidently considerably influenced by the nature of the solvent. While no extensive investigation was made of this effect, we have found that carbon tetrachloride entirely inhibits the reaction. Practically no reaction took place in 24 hours when 100 g. of trichloro-acetic acid and 58 g. of copper powder were stirred in boiling carbon tetrachloride under a reflux condenser. This is the more remarkable in view of the marked exothermic character of the reaction in benzene, ether or water, or in absence of any solvent. This question will receive further consideration in this Laboratory.

In this work, the yield of dichloro-acetic acid was determined by precipitating the aniline salt from the benzene solution of the acid, and weighing it. Actual yields as high as 85% were obtained. The best results were obtained by use of aniline trichloro-acetate in benzene rather than free trichloro-acetic acid.

Preparation of Aniline Dichloro-acetate from Aniline Trichloro-acetate.—Aniline trichloro-acetate is prepared by adding 55 g. of trichloro-acetic acid to 35 g. of aniline dissolved in 500 cc. of benzene in a 1-liter flask provided with a reflux condenser and stirrer. It is convenient to use a wide-mouth flask with a 3-hole cork stopper, having a funnel inserted through the third hole, through which the copper powder can be added from time to time without interrupting the stirring. The opening through the funnel is closed by a small cork except the copper powder is being added. The benzene is heated to boiling, the heating then stopped and 35 g. of copper powder is added in approximately 5g. portions at intervals of about five minutes. Stirring is continued for ten minutes after all the copper has been added.[6] A current of hydrogen chloride is then passed through the reaction mixture, which precipitates cupric and cuprous chlorides and aniline hydrochloride. The benzene solution of dichloro-acetic acid is filtered off, the hydrogen chloride is removed by drawing a current of air through the solution under diminished pressure, and 35 g. of aniline is added. Aniline dichloro-acetate, m. p. 122–123°, separates as a crystalline precipitate; yield, 75%.

The same procedure can be used with the omission of the first addition of aniline, but we have not been able to obtain more than a 50% yield, and we therefore recommend the method exactly described above.

Preparation of Dichloro-acetic Acid from Aniline Dichloro-acetate.—While this acid can be obtained from the benzene solution after saturating

---

[6] We have found the "dark copper bronze" used by decorators very satisfactory for this purpose. Indeed, we prefer it to any other form of finely divided copper that we have been able to secure.

the reaction mixture with hydrogen chloride and filtering, we have found it easier to obtain a pure acid by first preparing the aniline salt as just described and then decomposing it by hydrogen chloride in benzene suspension. The aniline dichloro-acetate is suspended in about thrice its weight of benzene, and hydrogen chloride is passed in to saturation. Aniline hydrochloride is precipitated and dichloro-acetic acid is formed, dissolved in benzene. After filtration, the filtrate is distilled. The benzene is removed and the pressure is then diminished, as the acid decomposes somewhat when distilled under atmospheric pressure. Pure dichloroacetic acid boils at 95–96° under 17.4 mm. pressure and at 102° under 20 mm. pressure.

Properties of Dichloro-acetic Acid.—In 1920 Pucher[7] studied Wallach's method of preparation of dichloro-acetic acid from chloral and alkali cyanide in aqueous solution, and we were fortunate in being able to secure from him a quantity of this acid prepared and purified by him. We have therefore determined some of the physical constants of dichloroacetic acid; (I) as received from Pucher; (II) the same, further purified by distillation under 17 mm. pressure; (III) acid prepared by us from pure aniline dichloro-acetate, m. p. 122–123°; (IV) acid prepared by us by saturating the benzene reaction mixture with hydrogen chloride, filtering and distilling, without purification through the aniline salt. Each of these samples gave an aniline salt melting at 122–123° when an equivalent amount of aniline was added to the acid in benzene solution. We have found that when appreciable amounts of trichloro-acetic acid are mixed with dichloro-acetic acid, the aniline salt that is precipitated gives a lower melting point when the amount is small and a higher melting point when the amount is large. These samples gave pure salt by simple precipitation and drying. Sample I was slightly yellow. The other samples were colorless.

The *boiling point* of dichloro-acetic acid is variously recorded. Wallach[8] gives 189–191°; Louguinine,[9] 194.42° under 760 mm. pressure; Maumené,[1] 195°; Perkin,[10] 194–195° (corr.); Patterson,[11] 99° under 20 mm. pressure; Pucher,[7] 102° under 20 mm. pressure. The results of our own determination agree with Pucher's value. We have not found the boiling point under normal pressure to be very significant. The product of distillation at atmospheric pressure always fumed strongly and contained some of the acid chloride. Phosgene and tarry products are also formed. When distilled at 17–20 mm. the product is colorless, does not fume and dissolves

[7] Pucher, THIS JOURNAL, **42**, 2251 (1920).

[8] Wallach, *Ber.*, **9**, 1213 (1876).

[9] Louguinine, *Ann. chim. phys.*, [7] **27**, 117 (1902).

[10] Perkin, *J. Chem. Soc.*, **65**, 422 (1894).

[11] Patterson, *Ber.*, **38**, 213 (1905).

in water without development of opalescence. Our boiling points under atmospheric pressure were taken with the thermometer entirely surrounded by the vapor, and ranged from 191° to 194.5°.

The *density* of dichloro-acetic acid has been determined by Perkin,[10] with the following results: d_4^4, 1.5843; d_{20}^{20}, 1.5707; d_{25}^{25}, 1.5604. For different samples, prepared by Pucher and by ourselves as stated above, our determinations ranged from d_{20}^{20} 1.5742 and d_4^{20} 1.5714 for Pucher's acid before redistilling, to d_{20}^{20} 1.5666 and d_4^{20} 1.5634 for our acid prepared from pure aniline dichloro-acetate and redistilled under 17 mm. pressure; b. p., 95–96°.

We have not found any record of the *refractive index* of dichloro-acetic acid. We have determined it for the four samples previously described, using an Abbé refractometer at 22° with the D line of sodium light. The tabulated results represent the mean of four settings of the instrument in each case.

Properties of Dichloro-acetic Acid

	I	II	III	IV
Boiling point at 760 mm., °C.....	191–194.5	191–194	192–193	192–193.5
Boiling point at 20 mm., °C......	102	102	102	102
Boiling point at 17 mm., °C......	....	....	95–96	....
Boiling point at 14 mm., °C......	93–94	....	....	....
d_{20}^{20}..........................	1.5742	1.5734	1.5666	1.5694
d_4^{20}..........................	1.5714	1.5670	1.5634	1.5666
n_D^{22}..........................	1.4678	1.4658	1.4659	1.4671
M. p. of aniline salt, °C..........	122–123	122–123	122–123	122–123

I. As obtained from Pucher.

II. The same redistilled at 20 mm.

III. Prepared by us from pure aniline dichloro-acetate.

IV. Prepared by us by distillation of benzene solution from reaction, after treatment with hydrogen chloride and filtering.

A short-stem thermometer was used throughout, to avoid the necessity of correction for exposed stem.

Summary

A method is described for the preparation of dichloro-acetic acid from trichloro-acetic acid and copper powder, or from aniline trichloro-acetate and copper powder. Yields up to 85% are obtained.

The acid thus prepared is compared with the acid obtained by Pucher from chloral and sodium cyanide. Values are given for boiling points, densities and refractive indexes of these preparations.

Amherst, Massachusetts