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The Reaction of Copper with Benzaldehyde

BY TENNEY L. DAVIS AND WALTER P. GREEN, JR.

When a piece of copper is boiled with benzaldehyde in an ordinary reflux apparatus from which air is not excluded, a portion of the metal dissolves to form a green or blue-green solution, and the solution deposits the metal again upon a different part of the flask if the boiling is continued. The reaction of aldehydes with the alkali metals and with others has been known for many years, the reaction of benzaldehyde with copper has been investigated more recently,[1] but the observation that copper is deposited from the boiling liquid appears to be new.

The present paper reports experiments which elucidate the reaction. Details of only a few typical experiments are given. Experiments which are thought to be sufficiently evident are not described in detail.

1. Copper is attacked by benzaldehyde in the presence of air, fairly rapidly at room temperature, more rapidly on warming, in the presence or in the absence of toluene or ethyl acetate, with the formation of cupric benzoate monobenzaldehyde monohydrate. This agrees with the earlier observation of Briggs, Saenger and Wardlaw.[2] No copper hydrobenzoin appears to be formed. In the absence of air or oxygen, copper is not attacked by pure benzaldehyde.

Nine grams of copper foil was allowed to stand with 16 g. of benzaldehyde in a large open test-tube at 50° for three days. It lost 0.4 g. in weight, and the solution on filtration yielded 2.6 g. of blue-green crystals. These, recrystallized from benzaldehyde, rinsed with toluene, sucked dry at the pump, and analyzed immediately, showed 14.81 and 14.73% of copper. The formulas, $(C_6H_5COO)_2Cu\cdot C_6H_5CHO\cdot H_2O$ and $(C_6H_5COO)_2Cu\cdot 2C_6H_5CHO$, correspond to 14.86 and 12.37% of copper, respectively. Organic solvents in general leach the benzaldehyde from the crystals leaving cupric benzoate as a blue powder. Mineral acids decompose them yielding the cupric salt of the acid, benzaldehyde and benzoic acid.

The anhydrous compound of cupric benzoate with one molecule of benzaldehyde was prepared by allowing 7 g. of cupric benzoate and 4.8 cc. of purified benzaldehyde to stand in an evacuated vessel for three days at 0°. The blue-green crystals were freed from the greenish liquor by pressing between tiles, and were analyzed at once. *Anal.* Calcd. for $(C_6H_5COO)_2Cu\cdot C_6H_5CHO$: Cu, 15.51. Found: Cu, 15.45, 15.59, 15.40.

Two pieces of copper foil, each weighing about 9 g., were heated separately with 14 g. each of purified benzaldehyde in nitrogen-filled sealed tubes at 180° for thirty-two days. They lost, respectively, only 0.0017 and 0.0019 g. in weight, results which we ascribe to the small amounts of oxygen or of oxidized benzaldehyde which were inadvertently present. The pale yellow liquids in the tubes evidently contained small amounts of cuprous benzoate, for they assumed a blue-green color on exposure to the air.

2. Hot benzaldehyde reduces cupric benzoate first to cuprous benzoate and later to metallic copper.[3] The reduction is more rapid with freshly purified benzaldehyde than with a slightly oxidized material from a bottle which has been opened and allowed to stand.

One gram of anhydrous cupric benzoate and 4 cc. of benzaldehyde (not especially purified) were heated in a sealed tube for fourteen hours at 190°. The solid product weighed 0.2232 g. and consisted of cuprous benzoate with a little copper. It was introduced into a tube and covered with a plug of cotton wool; a solution of 1 part of benzoic acid in 3 of xylene was introduced, and the tube was sealed. The liquid was warmed until the cuprous benzoate had dissolved; the tube was then inverted, whereby the cotton plug served as a filter to remove undissolved material, and the liquid on cooling deposited handsome white crystals of cuprous benzoate. These were washed thoroughly with ether and dried rapidly. In ether suspension the crystals oxidized quickly and turned green, but once dried they were found to be quite stable. The density of crystallized cuprous benzoate is 1.692 at 25°. When warmed slowly, it decomposes without melting; when warmed rapidly, it melts at 255° and decomposes immediately. *Anal.* Calcd. for C_6H_5COOCu: C, 45.52; H, 2.73; Cu, 34.42. Found: C, 45.73, 45.46; H, 2.87, 2.94; Cu, 34.25, 34.40.

(1) Smits and de Leeuw, *Koninkl. Akad. Wetenschappen Amsterdam*, 329 (1910), and de Leeuw, *Z. physik. Chem.*, **77**, 297 (1911), reported that copper and zinc and many other metals, but not silver, are attacked by acetaldehyde. Gates, *J. Phys. Chem.*, **15**, 138 (1911), noticed that benzaldehyde attacks copper at room temperature to form a green solution, but isolated no products. Bernoulli and Schaaf, *Helv. Chim. Acta*, **5**, 721 (1922), and Schaaf, *ibid.*, **6**, 535 (1923), *Z. allgem. Chem.*, **126**, 237 (1923), studied the rate of reaction of copper with benzaldehyde and reported that the copper salt of hydrobenzoin is formed, basing their conclusions merely on analysis and molecular weight determination without isolating hydrobenzoin itself. They also reported that magnesium, zinc, lead and silver dissolve in benzaldehyde, while iron, aluminum and nickel do not. Robinson, *Chem. Soc. Ann. Repts.*, **19**, 123 (1922), and a writer in *Ber. Schimmel and Co., Akt. Ges.*, 94 (1923), considered the formation of the copper salt of hydrobenzoin to be unlikely and unproved.

(2) Briggs, Saenger and Wardlaw, *J. Chem. Soc.*, 2552 (1931).

(3) Ciamician and Silber, *Ber.*, **48**, 187 (1915), reported that a benzene solution of benzaldehyde under the influence of light during six months reduces cupric benzoate to a mixture of cuprous benzoate and metallic copper, and considered the reaction to be photochemical. They separated the products mechanically, and reported the analysis of their cuprous benzoate: C, 44.61; H, 2.79; Cu, 35.08; calcd.: C, 45.52; H, 2.73; Cu, 34.42.

Mr. Thomas R. P. Gibb, Jr., of this Laboratory has kindly examined the crystals of cuprous benzoate and reports that they are rhombs of the monoclinic system, having positive birefringence and a fairly small optic angle, and showing uncentered optic axis interference figures together with occasional centered acute bisectrix interference figures.

Cupric benzoate heated at 190° for eighteen to twenty hours in a sealed tube with purified benzaldehyde gave metallic copper in the form of a powder consisting of small well-formed glistening crystals.

3. Metallic copper reacts with cupric benzoate in warm benzaldehyde solution in the absence (or with limited access) of air; the copper is attacked and dissolved, and the cupric benzoate is reduced to cuprous benzoate. On further warming the cuprous benzoate is reduced by the action of the benzaldehyde to metallic copper which deposits on the sides of the vessel or on any pieces of copper which may be present.

Forty grams of benzaldehyde, 2.3120 g. of anhydrous cupric benzoate, and 12.0224 g. of copper wire were heated together in a sealed tube at 210°. After one hour the reduction was not quite complete; the liquid was still of a bluish color. The heating was continued for twelve hours longer at the end of which time the liquid appeared pale yellow. The wire, after loosely adhering copper had been removed, was found to have lost 0.4548 g. in weight. The precipitate, which contained some cuprous benzoate, consisted largely of 1.2667 g. of metallic copper (insoluble in ammonia water).

A piece of copper foil, refluxed under an open air condenser with a solution of cupric benzoate in benzaldehyde, became coated with a heavy crystalline deposit of metallic copper. No detectable difference of electrical potential was found to exist between platinum and copper plates immersed in a boiling benzaldehyde solution of cupric benzoate; copper was deposited on the walls of the vessel and on the copper plate but not on the platinum.

4. Silver and mercury[4] are the only other metals which we have found to behave as copper does, to dissolve in hot benzaldehyde and after boiling to be deposited again in the metallic state. The peculiar "nobility" of these three metals, corresponding to their position in the periodic table, makes it probable that they are the only metals which behave in this way. Nickel, magnesium, tin, lead, zinc and bismuth dissolve readily in benzaldehyde in the presence of air, ordinary "iron" gauze (steel) does, pure iron wire, aluminum and tellurium only slightly, and platinum and gold not at all or extremely little.[5]

5. Copper is attacked fairly rapidly by butyraldehyde in the presence of air, and the resulting greenish-blue butyraldehyde solution of cupric butyrate on refluxing or on being heated in a sealed tube deposits metallic copper.

Conclusion.—The above-described experiments make it possible to explain the mechanism by which metallic copper is deposited again after it has been dissolved by heating with benzaldehyde in the presence of air. The cupric benzoate which is first formed reacts, in the absence (or with limited access) of air, either with the hot benzaldehyde solvent or with the metallic copper which remains unattacked, or with both, and is reduced to cuprous benzoate. The cuprous benzoate is then further reduced by the hot benzaldehyde to metallic copper.

Summary

The series of reactions by which copper dissolves in boiling benzaldehyde and later deposits again in the metallic state is explained.

Silver and mercury behave with benzaldehyde in the same manner as copper.

Copper behaves with butyraldehyde in the same manner as with benzaldehyde.

Nickel, magnesium, tin, lead, zinc, bismuth and ordinary impure iron are attacked by benzaldehyde in the presence of air to form salts which are not reduced to the metals by the further action of benzaldehyde.

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(4) Professor Avery A. Ashdown of this laboratory informs us that he observed several years ago that mercury is attacked rapidly by acetaldehyde in the presence of air. We have found that a mercury manometer used for measuring the vapor pressure of acetaldehyde and of butyraldehyde quickly became clogged with white crystals of mercuric acetate and butyrate [*cf.* THIS JOURNAL, **62**, 1272 (1940)].

(5) Bernoulli and Schaaf, *loc. cit.*, reported that copper, lead, zinc, silver, magnesium and cobalt are attacked, and nickel, iron and aluminum unattacked, by a 10% solution of benzaldehyde in toluene.