[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

REACTIONS OF VANILLIN AND ITS DERIVED COMPOUNDS. III.[1] THE CANNIZZARO REACTION OF VANILLIN[2]

IRWIN A. PEARL

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It has been a generally accepted fact that *ortho*- and *para*-hydroxybenzaldehydes, whether further substituted or not, are not amenable to the Cannizzaro reaction (1). Vanillin has been found to be no exception (2–5). In the first paper of this series it was demonstrated that vanillin underwent a Cannizzaro reaction with alkali in the presence of silver oxide to form vanillic acid and vanillyl alcohol, the latter in the form of its condensation product, 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane, and the former in an amount greater than 50% equivalent to the silver oxide present (6). All these reactions were accompanied by the simultaneous reduction of the silver oxide to a fluffy, porous metallic silver, and it was suspected that the metallic silver was the catalyst for the Cannizzaro reaction. The present paper pertains to a study of the reaction of vanillin with alkali in the presence of active silver metal (7).

Boiling for one hour of a solution of vanillin in excess 15% sodium hydroxide in the presence of 100 mole-% of dry fluffy silver (prepared by reducing silver oxide with vanillin and alkali, and having an apparent specific gravity of 0.90[3]) resulted in a quantitative Cannizzaro reaction with the formation of vanillic acid and polymerized vanillyl alcohol[4] in equivalent amounts. The same reaction in the presence of only 2 mole-% of the same silver yielded 19% of Cannizzaro reaction products and 80% of recovered vanillin, indicating that more silver surface was probably necessary for completion of the reaction in the 1-hour reaction time.

The effect of the type of silver metal upon the reaction was studied. A number of samples of silver metal having different apparent specific gravities and surface characteristics were prepared and tested under identical conditions

[1] For paper II of this series see Pearl, *J. Am. Chem. Soc.*, **68**, 1100 (1946).

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[3] The apparent specific gravity of the silver powder was obtained by tightly packing a 5-ml. volumetric cylinder with the powder and noting the weight. For those silver metals which could not be dried without fusion, the wet metal was packed into the volumetric cylinder and then quantitatively washed onto a tared sintered crucible and dried at 105°.

[4] It is recognized that the use of the term "polymerized vanillyl alcohol" for this product is not strictly correct according to the classical definition of "polymer," but the product does fall within the scope of the definition of "condensation polymer" (as distinguished from "association polymer") as used by Carothers [*J. Am. Chem. Soc.*, **51**, 2548 (1929)]. For want of a better term, "polymerized vanillyl alcohol" in this paper will refer to the alcohol product in various stages of polymerization (or polycondensation) as isolated from the reaction mixtures.

(as outlined above) as Cannizzaro reaction catalysts. Comparative results are shown in Table I.

The relationship of apparent specific gravity to the percentage of Cannizzaro reaction, together with the negative results obtained with the metallurgical

TABLE I

EFFECT OF TYPE OF SILVER ON CANNIZZARO REACTION OF VANILLIN

SOURCE OF SILVER USED	APPARENT SP. GR.	VANILLIC ACID, %	POLYMERIZED VANILLYL ALCOHOL, %	RECOVERED VANILLIN, %
Granular metallurgical	10.5	0	0	98.3
Heating of silver oxide	4.7	0	0	97.8
Reduction of silver nitrate with ferrous sulfate	1.56	16.6	14.3	71.1
Vanillic acid process—cold (6)	0.98	23.7	23.0	49.2
Vanillic acid process—hot (6)	0.90	50.0	50.0	0

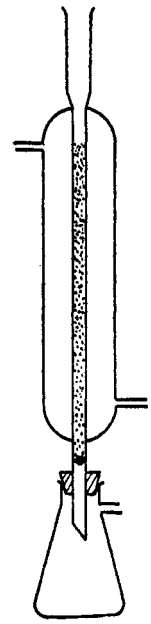


FIG. 1. APPARATUS FOR CANNIZZARO REACTION

types of silver, indicates that a large surface area is the requisite of a Cannizzaro reaction silver catalyst, the source of the finely divided silver having little effect. It appeared evident, therefore, that silver metals having apparent specific gravities less than 0.90 would catalyze the complete Cannizzaro reaction of vanillin either in a shorter reaction period or with a smaller silver-vanillin ratio. This proved to be the case.

The very fluffy silver obtained on oxidation of vanillin with alkali and silver

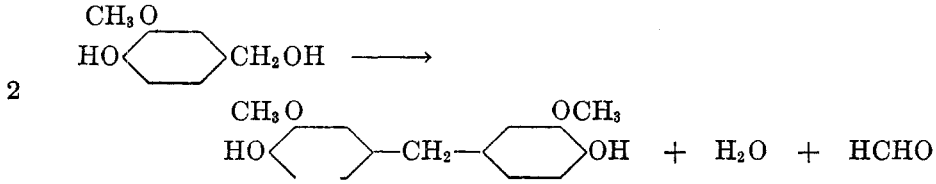
nitrate (8) caused complete reaction to take place in a few minutes at low temperatures and with low silver-vanillin ratios. The Cannizzaro reaction of vanillin with this freshly prepared catalyst always yielded an excess of vanillic acid over that called for by theory. This was due to the small amount of silver oxide present in the silver catalyst caused by oxidation with the sodium nitrate present in the reaction mixture (8). The silver catalyst did not lose its activity with reuse, and all succeeding experiments yielded vanillic acid and polymerized vanillyl alcohol in equivalent amounts.

The activity and stability of this fluffy silver made it ideal for use in a continuous Cannizzaro process. Passage of a hot dilute alkaline solution of vanillin over the heated catalyst in the apparatus pictured in Figure 1 resulted in a quantitative Cannizzaro reaction in as short a contact time as one minute. Catalysts with higher apparent specific gravities gave the desired results with longer contact times.

After it was found that vanillin would undergo the ordinary Cannizzaro reaction in the presence of active silver, the possible reduction of vanillin to vanillyl alcohol by means of the crossed Cannizzaro reaction with formaldehyde in the presence of silver was investigated. Davidson and Bogert (9) have proposed general directions for carrying out the crossed Cannizzaro reaction of aromatic aldehydes, in which the aldehyde is treated with 1.3 moles of formalin and excess alkali in methanolic solution. Addition of a mixture of vanillin and 1.3 moles of formalin to a stirred aqueous mixture of sodium hydroxide and active silver and boiling of the resulting mixture under reflux for 0.5 hour yielded only polymerized vanillyl alcohol and no vanillic acid. If the vanillin is dissolved in water containing one mole of alkali, treated with silver and 1.3 moles of formalin, and then with excess alkali, a substantial amount of vanillic acid is obtained in addition to the polymerized vanillyl alcohol.

The appearance of vanillic acid in the last experiment but not in the first indicated that an ordinary Cannizzaro reaction of vanillin might have taken place before addition of the formalin in the presence of active silver and only one mole of sodium hydroxide. This was confirmed by an experiment in which a solution of vanillin in water containing one mole of sodium hydroxide (enough to form the sodium salt) was treated with active silver; this yielded 30% of Cannizzaro reaction products.

The crossed Cannizzaro reaction of vanillin in the presence of silver with a formaldehyde-vanillin ratio of 5 to 1 yielded 82.5% of uncondensed vanillyl alcohol. This was the only experiment in the whole study which yielded vanillyl alcohol in an unpolymerized form. In the case of the crossed Cannizzaro reaction of vanillin, the following reaction also operates (6). Although this reaction



is not reversible, it is evident that a large excess of formaldehyde actually prevents the reaction from taking place.

All attempts to obtain a crossed Cannizzaro reaction without the silver catalyst failed completely.

EXPERIMENTAL

All melting points given are uncorrected.

Reaction of vanillin with alkali in presence of active silver. A suspension of 21.6 g. (0.2 atom) of dried fluffy silver metal [from vanillin oxidation with silver oxide and alkali (6)], having an apparent specific gravity of 0.90, in 250 cc. of water was treated successively with 40 g. (1.0 mole) of sodium hydroxide and 30.5 g. (0.2 mole) of vanillin. The mixture was heated to boiling under reflux for one hour, filtered, and the silver was thoroughly washed with water. The cooled filtrate and washings were acidified with carbon dioxide and extracted with ether. The ether was dried and distilled to yield 13.3 g. (50%) of a yellow resinous solid which was recrystallized from water to give white needles of 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane, melting at 108–109° and not lowering a mixed melting point with authentic 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane. In addition, some uncrystallizable resinous polymeric material was obtained. The aqueous carbonated layer was acidified with dilute sulfuric acid and extracted with ether. This yielded 16.8 g. (50%) of vanillic acid which, upon recrystallization from water, melted at 210–211°. An alternate method gave substantially identical results. The original filtrate and washings were acidified with sulfur dioxide and extracted with ether. The ether was extracted with 8% sodium bicarbonate solution, dried and distilled to give the polymerized vanillyl alcohol product, part of which could be recrystallized from water to give the dihydroxydimethoxydiphenylmethane. Acidification and ether extraction of the bicarbonate extract yielded vanillic acid.

The above reaction was repeated in the presence of only 2 mole-% of the same silver catalyst. Yields of 9.6% vanillic acid, 9.5% polymerized vanillyl alcohol, and 80% recovered vanillin were obtained.

Effect of type of silver on Cannizzaro reaction of vanillin. The following metallic silvers were prepared and used in the experiment outlined above. Results are given in Table I.

Granular metallurgical silver was screened to pass a 10-mesh sieve. The apparent specific gravity was 10.5.

Finely divided silver was prepared by heating silver oxide. The latter was formed by treating a solution of 34 g. of silver nitrate with an aqueous solution of 8 g. of sodium hydroxide. The precipitated oxide was filtered, washed free of nitrate with water and dried at 110°. The oven-dried oxide was then heated above 300°, when the brownish black oxide changed to a white shiny metal. The granular metal was suspended in water and mixed in a Waring Blendor for several minutes. The very fine white powder of pure silver obtained had an apparent specific gravity of 4.7.

Finely divided silver having an apparent specific gravity of 1.56 was prepared by treating a boiling solution of 34 g. of silver nitrate in 125 cc. of water with ferrous sulfate solution until all the brown precipitate which formed redissolved. The silver was deposited as a gray, finely divided precipitate; this was filtered, washed with dilute hydrochloric acid, then with water, and dried at 110°.

Two fluffy silver metals were prepared by adding vanillin to aqueous alkaline suspensions of silver oxide at 55° and at 35° as described in an earlier paper (6). These silver metals had apparent specific gravities of 0.98 and 0.90, respectively.

Reaction of vanillin with alkali in presence of very active silver. The wet spongy silver (43.2 g.) (0.4 atom), formed by adding a solution of 0.4 mole of silver nitrate to an alkaline solution of vanillin at 55° (8) and having an apparent specific gravity of 0.2, was covered with 800 cc. of water and treated with 96 g. (2.4 moles) of sodium hydroxide. The mixture

was cooled to 30° and 60.8 g. (0.4 mole) of vanillin was added. The temperature rose to 38°. After 10 minutes the mixture was filtered and the silver was washed thoroughly with water and stored under water. The filtrate and washings were acidified with sulfur dioxide and worked up as described above. Yields of 40.2 g. (59.8%) of vanillic acid and 20 g. (37.8%) of polymerized vanillyl alcohol were obtained.

The spongy silver obtained in this experiment was employed in another identical experiment, but the yields were 33.4 g. (49.6%) of vanillic acid and 25.3 g. (47.6%) of polymerized vanillyl alcohol.

This reused spongy silver also catalyzed substantially quantitative Cannizzaro reactions of vanillin with silver-vanillin mole ratios of one to ten in 15 minutes.

Continuous Cannizzaro reaction of vanillin. A reaction column was prepared from a 30-cm. Pyrex Liebig condenser. A constriction was made two inches from the lower end and a plug of steel wool was inserted through the top. The column was packed with wet active spongy silver (apparent specific gravity, 0.17) and steam was circulated through the condenser jacket. A filter flask was used as a receiver. A hot solution of 30.4 g. (0.2 mole) of vanillin and 48 g. (1.2 moles) of sodium hydroxide in one liter of water was slowly added at the top of the column. The receiving flask was connected to the water-pump and a slight vacuum was applied. The vacuum was adjusted so that the alkaline vanillin solution was in contact with the catalyst for approximately one minute. After all the solution had passed, the column was washed with water. The percolate and washings were acidified with sulfur dioxide and extracted with ether. The ether was dried and distilled, leaving a mixture of white crystals and yellow solid which was then shaken with 8% sodium bicarbonate solution and filtered. The precipitate of polymerized vanillyl alcohol (melting at 95–100°) weighed 13 g. (46.9%). The sodium bicarbonate solution was acidified with dilute sulfuric acid giving a white granular precipitate. The mixture was extracted with ether and worked up as before to yield 16.8 g. (50%) of vanillic acid melting at 207–210°.

This experiment was repeated many times with the same catalyst and the catalyst did not lose any of its activity.

Active silver catalysts, prepared by the silver oxide process at 55° (6) and having apparent specific gravities of approximately 0.90, could be used in the continuous process, but contact times of about 10–20 minutes were necessary for complete transformation of the vanillin.

Crossed Cannizzaro reaction of vanillin. A stirred suspension of 21.6 g. (0.2 atom) of spongy silver, having an apparent specific gravity of 0.17, in a solution of 48 g. (1.2 moles) of sodium hydroxide in 450 cc. of water at 40° was treated with a thin paste of 30.4 g. (0.2 mole) of vanillin, 20.0 cc. (0.26 mole) of 37% formalin, and 50 cc. of water. The resulting mixture was gradually heated to boiling under reflux and mercury-sealed stirring and refluxed for 30 minutes. After cooling, the mixture was filtered and the silver was washed well with water. The filtrate and washings were saturated with carbon dioxide, then saturated with sodium chloride and extracted with ether. The ether was dried and distilled to yield 25.5 g. (96.2%) of polymerized vanillyl alcohol as a light yellow resin. Recrystallization of this material from ligroin or water yielded white crystalline products with indefinite melting points ranging from 65–110°. No vanillic acid could be found in the carbonated solution.

The same reactants were employed in an entirely different reaction procedure. A solution of 0.2 mole of vanillin and 0.2 mole of sodium hydroxide in 450 cc. of water was first treated with 0.2 atom of silver (from the last experiment) and then with 0.26 mole of formalin. One mole of solid sodium hydroxide was added with vigorous stirring and the mixture was heated to boiling under reflux as above. The reaction mixture was worked up in the same manner as the last experiment. Yields of 8.8 g. (26%) of vanillic acid and 18.7 g. (71%) of polymerized vanillyl alcohol, were obtained.

Crossed Cannizzaro reaction of vanillin with large excess of formaldehyde. A mixture of 21.6 g. (0.2 atom) of active silver (from the last experiment), 100 cc. of water, and 24.0 g. (0.6 mole) of sodium hydroxide was blended in a Waring Blendor. The temperature of the

mixture at this point was approximately 45–50°. Without agitation, a mixture of 15.2 g. (0.1 mole) of vanillin and 50 cc. (0.5 mole) of 37% formalin was added and the Blendor was turned on. The temperature rose gradually until after 30 minutes it reached 85°, where the silver suddenly became light colored and very heavy. The mixture was filtered and the silver washed with water. The silver was hard and had an apparent specific gravity of 4.1. The combined filtrate and washings were saturated with carbon dioxide and sodium chloride and then extracted with ether. The ether solution was dried and distilled, leaving 12.7 g. of light yellow oil which crystallized on standing to white prisms melting at 105–112°. Recrystallization from benzene gave needles melting at 114–115° and not depressing the m.p. of a mixture with authentic vanillyl alcohol. The yield was 82.5%. Acidification of the carbonated aqueous layer and subsequent ether extraction yielded a little more vanillyl alcohol and 1.2 g. (7.1%) of vanillic acid melting at 209–210°.

SUMMARY

Active silver metal catalyzes the quantitative Cannizarro reaction of vanillin, to yield equivalent amounts of vanillic acid and polymerized vanillyl alcohol. Active silver also catalyzes the crossed Cannizzaro reaction of vanillin with formaldehyde to yield only polymerized vanillyl alcohol. A crossed Cannizzaro reaction with excess formaldehyde yields unpolymerized vanillyl alcohol.

APPLETON, WIS.

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