

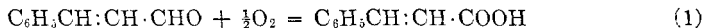
NOTE ON THE OXIDATION OF CINNAMALDEHYDE

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The oxidation of benzaldehyde to benzoic acid is known to proceed through the stage of the peroxide, but the final result is the simple addition of oxygen to form the acid. The oxidation of cinnamaldehyde probably proceeds through similar intermediate stages; it is slower than that of benzaldehyde, and the final result is more than the simple addition of oxygen according to the equation,



Much more than this amount of oxygen was used up by the cinnamaldehyde in the authors' experiments. Also carbon dioxide was formed as the oxidation proceeded, the rate of production of the carbon dioxide increasing with the time. Approximately 0.2 volume of carbon dioxide was formed while 1 volume of oxygen was absorbed; and 1 g. of cinnamaldehyde absorbed 220 cc. of oxygen, though oxidation was still uncompleted. (According to equation 1, 1 g. of cinnamaldehyde forms 1.12 g. of cinnamic acid and absorbs 85 cc. of oxygen; all gas volumes in this paper are at N.T.P.)

Moreover formic acid vapor was smelt—and confirmed—after the oxidation of some cinnamaldehyde in a closed vessel. The smell of benzaldehyde also was noticed at the end of similar oxidations. Among the oxidation products of a large amount of the cinnamaldehyde were found formic, benzoic, and acetic acids, which were roughly estimated: 100 parts of cinnamaldehyde gave 107 parts of cinnamic acid (maximum value), 0.7 part of benzoic acid, 4.5 parts of formic acid, and 0.4 part of acetic acid.

This work must be regarded only as preliminary work indicating that the oxidation of cinnamaldehyde proceeds in a complex manner. Experiments are needed on the oxidation of pure (100 per cent) cinnamaldehyde in pure oxygen, dry and moist, with and without removal of the carbon dioxide as it is formed, and in the presence or absence of the other products of the oxidation. It may be mentioned that benzaldehyde has been detected when cinnamaldehyde is oxidized by potassium permanganate (solutions), both by the authors and by Nicholls (3), and by others; that

the accelerating effect of cinnamic acid on this oxidation is supported by the work of Almquist and Branch (1); and that acetic acid has been found in similar oxidations (2).

EXPERIMENTAL

The stock cinnamaldehyde, from Givaudan and Co., France, was colored yellow. The amount of cinnamic acid in this increased slowly from 4.5 to 7 per cent in three years. Some of the aldehyde was distilled in vacuo; after one such distillation the acid content was 2.0 per cent, and after a second distillation 0.85 per cent. All the acid figures quoted were found by titrations in alcoholic solution with carbonate-free caustic soda solution, using phenolphthalein, and the results were calculated as cinnamic acid.

Gasometric experiments

Cinnamaldehyde was dropped on to a filter paper placed at the closed end of a eudiometer, which had been filled previously with dry oxygen; the eudiometer was then inverted over mercury, some air being introduced in these operations. Then the volume of the gas was read during the following days and reduced to N.T.P. The first diminution of gas was rapid, but finality was long delayed. The volume of absorbed oxygen was greater than that calculated from equation 1. Also the titration of the final product indicated a quantity of acid which, assumed to be all cinnamic acid, should have resulted from a smaller volume of oxygen than that absorbed. Some typical experiments were as follows:

(1) The original aldehyde used (stock) = 0.1712 g. In this the acid content = 0.0099 g. Thus the net aldehyde = 0.1613 g. \equiv 13.7 cc. of oxygen, by equation 1. The original gas = 44.3 cc. (probably 80 per cent oxygen). The contraction equalled 14.2 cc. after 2 days, 18.7 cc. after 10 days, and 20.0 cc. after 19 days. The "contraction" may be low, owing to oxidation before the volume can be read at the start and to presence of carbon dioxide, here unmeasured. The acid formed by the oxidation, calculated as cinnamic acid, was 0.1513 g., which equals 11.5 cc. of oxygen (equation 1). In this experiment the oxygen was in excess.

(2) The original aldehyde (distilled) = 0.4241 g. In this the acid content = 0.0085 g. Thus the net aldehyde = 0.4156 g. \equiv 35.3 cc. of oxygen (equation 1). The original gas = 43.7 cc. The gas remaining was 11.9 cc. after 3 days, 12.2 cc. after 4 days, and 12.7 cc. after 7 days. The volume of 12.7 cc. consisted of 6.2 cc. of carbon dioxide and 6.5 cc. of nitrogen.

(3) An oxidation was carried out as above, except that samples of the gas were removed at intervals and were analyzed for oxygen and carbon dioxide. This experiment proved that the production of carbon dioxide

increased during the course of the oxidation. The first action is probably represented by equation 1, followed by side reactions.

(4) An experiment similar to experiment 2 was carried out with 0.355 g. of cinnamaldehyde spread over 0.2 g. of cinnamic acid in filter paper. This indicated a rather more rapid oxidation reaching the same stage as the final stage of experiment 2 in 2 days. The presence of cinnamic acid therefore may accelerate the side reactions.

(5) An experiment similar to experiment 1 was carried out with benzaldehyde. The benzaldehyde used = 0.3734 g. In this the benzoic acid content = 0.0084 g. Thus the net benzaldehyde = 0.3650 g. \equiv 38.2 cc. of oxygen (equation 1). The contraction = 36.0 cc. after 1 day, and 36.1 cc. after 3 days. Titration of the final product indicated 0.3967 g. of benzoic acid, which corresponds to 36.4 cc. of oxygen. Benzaldehyde therefore oxidizes in the normal manner.

(6) In four experiments like experiment 2 the oxidation was started over mercury, and subsequently the carbon dioxide was removed by the introduction of caustic potash solution. The volumes of carbon dioxide produced per volume of oxygen absorbed were 0.166 (in 7 days, experiment 2), 0.198 (in 2 days, experiment 4), 0.213 and 0.225 (both in 6 days); mean value, 0.2. But this ratio of course will vary throughout the oxidation.

(7) This experiment was done with caustic potash solution over the mercury in the eudiometer throughout. The gas volumes were corrected for the vapor pressure of the caustic potash solution as well as for temperature and pressure; the temperature varied from 8°C. to 26°C., and the gas was kept, as usual, at about the atmospheric pressure, i.e., about 725 mm. The used cinnamaldehyde (distilled) = 0.2433 g. In this the acid content = 0.0019 g. Thus the net aldehyde = 0.2414 g. \equiv 20.5 cc. of oxygen. The gas volume was read over six months, and the following results are selected:

Time, in days.....	0	1	3	7	14	25	50	102	130	158	184
Contraction, or volume of gas absorbed, in cc.....	0	18.5	24.7	31.9	36.9	41.5	44.4	47.9	49.6	50.65	51.4

The final ratio, $\frac{\text{Oxygen used}}{\text{Oxygen per equation 1}}$, is 2.51. In this experiment the oxygen was in excess throughout.

In a similar experiment the last ratio was 2.69 (over 190 days). This oxidation was probably completed; the final product had no smell of cinnamaldehyde, but it had a distinct smell of benzaldehyde.

(8) Similar gasometric blank experiments with the filter paper, in the presence or absence of cinnamic acid, and in oxygen either dry or over

caustic potash solution, showed no diminution in the volume of gas, i.e., no oxidation, for at least eighty days.

A large-scale oxidation

Cinnamaldehyde was placed in an open weighing bottle in a large vessel which was filled with dry oxygen. This aldehyde had been separated from the stock sample as bisulfite compound, regenerated, and distilled in vacuo; but it had been kept for twelve months in a desiccator before this experiment was started.

The original aldehyde = 20.94 g. In this the acid content = 1.54 g. Thus the net aldehyde = 19.40 g. In oxygen the gain in weight after 18 days = 0.42 g.; after 28 days = 0.54 g.; after 52 days = 0.98 g. In air the gain in weight after 74 days = 1.13 g. The total possible gain in weight according to equation 1 is 2.35 g.; in the experiment the oxidation is therefore about half completed. Also the gain of 1.13 g. corresponds to 10.45 g. of cinnamic acid according to equation 1. The

TABLE 1
Changes in the physical constants of cinnamaldehyde on oxidation

PER CENT CINNAMIC ACID IN THE ALDEHYDE	DENSITY	VISCOSITY	DENSITY	REFRACTIVE INDEX
5.20	1.0492	0.0470	—	—
5.78	1.0506	0.0486	—	—
0.9	—	—	1.055	1.6217
7.0	—	—	1.064	1.6207
13.9	—	—	—	1.6179

resulting acid crystals were separated from the liquid; the crystals weighed 8.7 g., and the liquid 13.4 g. As cinnamaldehyde saturated with cinnamic acid contains about 15 per cent of the latter, the liquid contains 2 g. of the acid, which therefore is the main product of the oxidation. The liquid was shaken with excess of caustic soda solution, and the emulsion was then shaken with ether. The aqueous layer was acidified, when 1.0 g. of aromatic acids was recovered; this product contained 5 per cent of benzoic acid, and the remainder was mostly cinnamic acid. The separated aqueous solution contained benzoic acid (0.01 g.), formic acid (0.4 g.), acetic acid (0.04 g.), and cinnamic acid (about 0.1 g. = saturated solution). The ethereal extract gave on distillation 8 g. of cinnamaldehyde and a higher boiling residue (aldehyde plus cinnamic acid plus any other products of oxidation and impurities). This residue was 1.3 g. Calling it cinnamic acid, the products accounted for were 11.1 g. of cinnamic acid, 0.06 g. of benzoic acid, 0.4 g. of formic acid, and 0.04 g.

of acetic acid, besides 8 g. of unchanged aldehyde; total = 19.6 g. The 22.1 g. of product thus would contain 9.1 g. of aldehyde, 12.5 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid. Allowing for the acid in the original aldehyde and for the unchanged aldehyde, it was found therefore that 10.3 g. of aldehyde (net) oxidized to 11.0 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid, besides the carbon dioxide found in the gasometric tests, and other probable products. There was found no oxalic acid among the oxidation products, and no formalin.

Benzoic acid was detected by the smell of ethyl benzoate and was estimated approximately by Nicholls' method (3). Acetic acid was detected by the smell of ethyl acetate and was estimated by distillation and titration and by afterwards checking the weight of the equivalent lead acetate. Formic acid was estimated by weighing the mercurous chloride reduced from mercuric chloride.

It was found that the crystals produced from the oxidation of cinnamaldehyde, although washed with benzene or carbon tetrachloride and subsequently dried for months in desiccators, only contained about 96 per cent cinnamic acid. Evidently small amounts of cinnamaldehyde become entangled and occluded in the crystals and final oxidation of these to acid is very slow. Melting-point determinations and a combustion analysis confirmed this supposition.

After titrating some oxidation crystals, which went 97 per cent cinnamic acid, the alcohol was distilled off, and the residue was extracted with ether. From the aqueous solution then the cinnamic acid was reprecipitated by adding hydrochloric acid; after washing well with water and drying in vacuo over sulfuric acid, the crystals analyzed 100.5 per cent cinnamic acid. Probably a trace of benzoic acid caused this high result.

As cinnamaldehyde oxidizes and holds more cinnamic acid in solution, the density and viscosity rise and the refractive index falls. Typical results are given in table 1.

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