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## THE ABSORPTION OF OXYGEN BY BENZALDEHYDE

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## Introduction

The reaction of oxygen with benzaldehyde has been the subject of much investigation since the time of Wöhler and Liebig,<sup>1</sup> who observed that benzaldehyde is converted into benzoic acid in air, more rapidly in the light. Excellent historical reviews of the general subject of autoxidations have been prepared by Moureu and Dufraisse<sup>2</sup> and by Jorissen and Belinfante.<sup>3</sup> Bibliographies more particularly concerned with this reaction may be found in recent papers by Jorissen and van der Beek,<sup>4</sup> Bäckström and Beatty,<sup>5</sup> and Raymond.<sup>6</sup> Since these lists are practically complete it is unnecessary to repeat all of the references here.

The reaction has aroused much interest because it has been found that traces of other substances may either accelerate or inhibit the absorption. The influence of an inhibitor disappears after a period of time during which the inhibitor is itself oxidized, even though it may be a substance that in the pure state would not be affected appreciably by oxygen.

Apart from the influence of inhibitors and accelerators many peculiarities have been found in the reaction. These may be summarized as follows. (1) The reaction is photosensitive. (2) The reaction is probably a chain reaction both in the dark and in the light. (3) Earlier rate measurements have usually shown an induction period. (4) The rate constantly diminishes as time proceeds. (5) The walls of the containing vessel seem to play a part in the reaction, although there is little agreement on this point among investigators. (6) The reaction is presumably an excellent example of consecutive reactions, the first step being the formation of an intermediate peroxide, the second step the interaction of the peroxide with benzaldehyde to form benzoic acid.

We have investigated to some extent the influence of change of oxygen pressure on the rate of the reaction, but our chief efforts have been directed toward determining the distribution of absorbed oxygen between peroxides and benzoic acid during the reaction at a constant pressure of oxygen. In the present paper we shall report on the results obtained when, as far as possible, only benzaldehyde, oxygen and the products of their interaction are present.

<sup>1</sup> Wöhler and Liebig, *Ann.*, **3**, 253 (1832).

<sup>2</sup> Moureu and Dufraisse, *Chem. Rev.*, **3**, 113 (1927).

<sup>3</sup> Jorissen and Belinfante, *Rec. trav. chim.*, **48**, 711 (1929).

<sup>4</sup> Jorissen and van der Beek, *ibid.*, **49**, 138 (1930).

<sup>5</sup> Bäckström and Beatty, *J. Phys. Chem.*, [9] **35**, 2530 (1931).

<sup>6</sup> Raymond, *J. chim. phys.*, **28**, 480 (1931).

### Materials

**Benzaldehyde.**—The benzaldehyde was purified by many fractional distillations in a current of dry carbon dioxide gas. The apparatus was so arranged that as many fractionations as desired could be obtained without contact between the benzaldehyde and air, stopcocks or rubber. The purification was continued until the usual induction period in the reaction of benzaldehyde with oxygen had disappeared. The product was stored in the dark under an excess pressure of carbon dioxide, in a flask so constructed as to permit a stream of gas to pass through and prevent the entrance of air when opened for the removal of samples.

**Benzoic Acid.**—Benzoic acid of a high grade was repeatedly recrystallized from water and dried over calcium chloride.

**Oxygen.**—The oxygen was obtained from a commercial manufacturer. Analysis showed it to contain more than 99.5% oxygen.

**Variation of the Rate with the Oxygen Pressure.**—When pure benzaldehyde is shaken at a constant speed in the dark and in contact with a fixed volume of oxygen, the rate of change of the logarithm of the oxygen pressure decreases with time much faster than would be expected from the using up of the benzaldehyde to form benzoic acid. Milas<sup>7</sup> has explained similar results in other autoxidations by assuming the removal of the active substance by an induced polymerization. This explanation is not valid in the case of benzaldehyde. On analyzing for the benzaldehyde left after the reaction had decreased considerably in rate, we found it to be practically equal to the original quantity less the benzaldehyde converted to benzoic acid and peroxides.

When similar experiments were performed with benzaldehyde containing 3% of benzoic acid the rate of change of the logarithm of the oxygen pressure was, after the first few minutes, slightly more constant than would be expected from the decrease in the concentration of the benzaldehyde. The reaction between benzaldehyde and oxygen is, therefore, of the first order with respect to oxygen. The rate is decreased probably by the action of small quantities of substances produced in the reaction. In the presence of benzoic acid the formation of these inhibitors is prevented or they rapidly reach a steady state concentration.

Table I shows the data from an experiment on the autoxidation of a benzaldehyde-benzoic acid mixture, the rate of reaction being measured by the decrease of the oxygen pressure with time. The total oxygen absorbed corresponded to 55 cc. at 25° and 760 mm. of mercury. The initial benzaldehyde and benzoic acid were equivalent to 263 cc. and 9.1 cc. of oxygen, respectively. The rate constant was calculated as  $K = d \log_{10} P/dt$ , where  $P$  is the oxygen pressure in mm. of mercury and  $t$  is the time in minutes.

<sup>7</sup> Milas, *THIS JOURNAL*, **52**, 734 (1930).

TABLE I  
DATA ON THE REACTION OF A BENZALDEHYDE-BENZOIC ACID MIXTURE WITH A CONSTANT VOLUME OF OXYGEN

Time in minutes	Pressure of oxygen in mm.	$K \times 10^3$	Time in minutes	Pressure of oxygen in mm.	$K \times 10^3$
0	753.0		50	530.5	6.74
11	693.5	7.48	60	495.0	6.93
20	651.5	6.95	70	463.0	6.67
30	608.0	6.90	80	433.0	6.69
40	567.5	6.88			

**The Distribution of Absorbed Oxygen.**—The absorption of oxygen gas and the quantities of benzoic acid and of peroxides formed were measured during the reaction at 25° and 1 atmosphere pressure of oxygen and in the absence of light. The more important parts of the apparatus used are shown in Fig. 1.

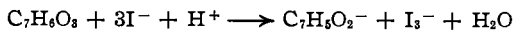
The automatic gas buret, C, was filled with oxygen just before starting an experiment and then closed off from the remainder of the apparatus until needed. The buret was kept at a temperature of 25° by a water jacket and a water circulating system.

The reaction vessel, B, was immersed in a thermostat filled with water blackened by the addition of India ink. Before each experiment the vessel was thoroughly cleaned and steamed out. It was charged with a 2.25-cc. portion of benzaldehyde or a benzaldehyde-benzoic acid mixture under an atmosphere of carbon dioxide. The container above the reaction vessel was filled with a solution of potassium iodide in methyl alcohol and water. This solution was readily miscible with the autoxidized benzaldehyde.

The manometer, D, connected to the gas buret, C, was so adjusted that a very slight fall in pressure caused an electrical circuit to be broken. By the use of electric switches, etc., the breaking of the circuit was caused to activate a mechanism for lifting the mercury bottle, E. When the pressure in the system was restored to 1 atmosphere the circuit in D again closed and the ascent of E automatically stopped. The mechanism for raising E was composed of an electric motor, a speed-reducing gear and a small rotating shaft upon which a cord attached to E was wound. The manometer controlled the pressure with a variation of about 0.2% during the course of a reaction.

Reactions were started by filling the reaction vessel with oxygen after evacuating other gases, connecting in the gas buret and then shaking the vessel by the use of a mechanism driven by a constant speed motor. The time elapsed from the admission of oxygen until the shaker was started was three to five seconds. The volume of oxygen absorbed was noted at short intervals.

At a chosen time the potassium iodide solution was run into the reaction vessel and the shaker stopped. The iodine liberated by the action of the peroxides was titrated with sodium thiosulfate solution and, following this, the benzoic acid was titrated with sodium hydroxide solution. It was assumed that the following reaction took place on adding the potassium iodide solution to the contents of the reaction vessel.



Each equivalent of iodine represents half a mole of peroxide and the loss of half a mole of acid. This benzoic acid was added to that found later by the titration with standard alkali. On this basis the absorbed oxygen in the form of peroxides and benzoic acid at the instant of the stopping of the reaction was calculated. That these assumptions give essentially the correct results is shown by the facts that the initial rate of formation of peroxides is equal to the rate of absorption, while the initial rate of formation of benzoic acid is practically zero, and that the sum of the peroxide and benzoic acid oxygen is

approximately equal to the oxygen absorbed. When necessary in the early stages of the reaction, known quantities of benzoic acid were added to the potassium iodide solution to furnish the required acid for the above reaction.

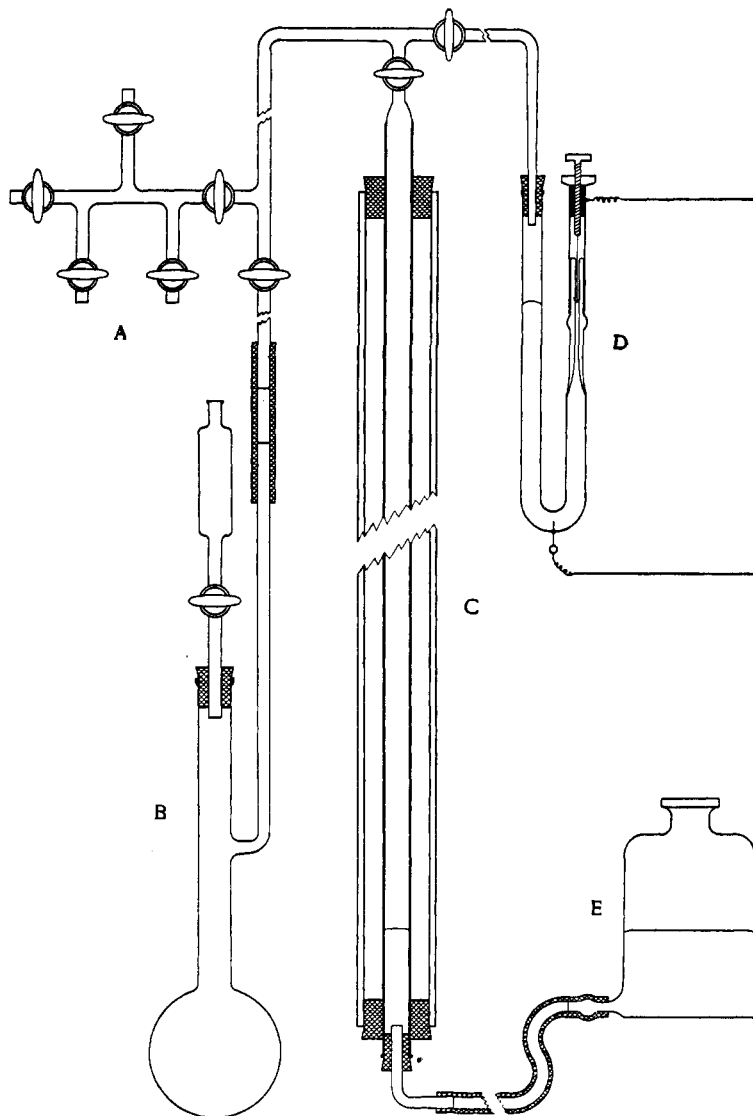


Fig. 1.—Automatic gas buret used for measuring the oxygen absorbed at constant pressure: A, connections to oxygen supply, manometer, vacuum pump and vent; B, reaction vessel and container for potassium iodide solution; C, buret tube with constant-temperature water jacket; D, mercury manometer which controls the mechanism for raising the mercury bottle; E, mercury bottle.

The sum of the peroxide and benzoic acid oxygen averaged about 3% less than the oxygen measured volumetrically. This discrepancy is probably real and due to the formation of substances not included in our analysis. Some indication of an unknown side reaction is found in the fact that benzaldehyde which has undergone extensive autoxidation acquires a yellow color and may produce small amounts of a yellow solid.<sup>8</sup>

In an effort to secure an explanation of this oxygen discrepancy we searched for the following substances: benzil, phenolic materials, carbon dioxide, carbon monoxide, peroxides that react rapidly with iodide ion only in strongly acid solution and peroxides that lose oxygen gas in the presence of iodide ion. All of these were found to be absent and would have been detected readily if present in quantities sufficient to explain the disagreement in our measurements.

In our method the complete time curve for the absorption of oxygen could be obtained by a single experiment, while the amounts of peroxides and benzoic acid could only be obtained for a particular instance by one experiment. It was necessary to perform many experiments over varying intervals of time in order to secure the data for the construction of the peroxide and benzoic acid time curves. The absorption time curve shown in Fig. 2 was taken from one of the faster reactions which was chosen as a standard. The unshaded points along this curve are those of the standard reaction, while the shaded points indicate the final total absorptions of the separate reactions. In some cases the results were weighted according to the agreement of the reaction with the standard. The results of the experiments started with the purified benzaldehyde are shown in Table II. The curves for the total absorption, the formation of benzoic acid, the formation of peroxides and the difference between the calculated and the

TABLE II

## DATA ON THE REACTION OF THE PURIFIED BENZALDEHYDE WITH OXYGEN

Time of reaction, min.	Total absorption, cc.	Oxygen as peroxide, cc.	Oxygen as benzoic acid, cc.	Total oxygen by analysis, cc.	Oxygen discrepancy, cc.
6.02	9.35	8.05	1.17	9.22	0.13
8.00	11.30	9.05	2.45	11.50	— .20
12.50	17.22	13.75	3.26	17.01	.21
16.32	20.88	15.13	5.50	20.63	.25
19.78	26.00	16.65	8.85	25.50	.50
24.00	27.40	15.38	11.12	26.50	.90
28.00	32.80	13.34	18.82	32.16	.64
30.12	36.65	12.09	23.98	36.07	.58
35.18	38.50	10.25	27.00	37.25	1.25
36.40	42.32	9.23	32.12	41.35	0.97
40.20	43.20	7.95	34.25	42.20	1.00
41.39	45.80	7.63	36.20	43.83	2.03
43.50	48.60	6.76	39.95	46.71	1.89
47.00	48.62	6.20	40.50	46.70	1.92
60.58	65.43	5.51	58.02	63.53	1.90
61.78	63.00	5.45	55.48	60.93	2.07

<sup>8</sup> A similar substance has been noted by Bäckström and Beatty in the autoxidation of mixtures of benzaldehyde and anthracene.

observed oxygen are shown in Fig. 2. All results are expressed in terms of volumes of oxygen at 25° and 760 mm. of mercury.

It is apparent from Fig. 2 that the benzoic acid is formed in a follow reaction between the peroxide and the benzaldehyde. The results also

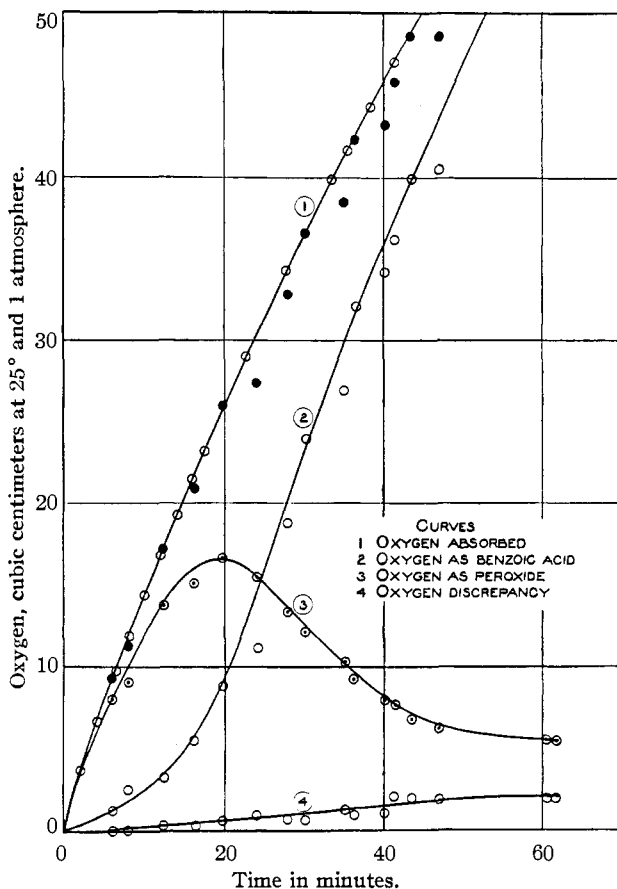


Fig. 2.—Reaction of purified benzaldehyde: curves showing the variation with time of, 1, the total oxygen absorbed, 2, the oxygen used to form benzoic acid, 3, the oxygen in the form of peroxides and, 4, the discrepancy between the volume of oxygen absorbed and the oxygen accounted for by analysis.

show that the rate of this reaction increases markedly as the reaction proceeds. Thus the rate of formation of benzoic acid is 0.3 cc. of oxygen per minute when 9.0 cc. of peroxide oxygen is first present, but it is 1.2 cc. per minute when the peroxide is again present in this amount in a later stage of the reaction. The increase in the rate is apparently due to the presence of benzoic acid. This relation was tested further by adding

benzoic acid equivalent to 9.1 cc. of oxygen in the usual charge of benzaldehyde. The data from these experiments are presented in Table III and Fig. 3 in the same manner as before.

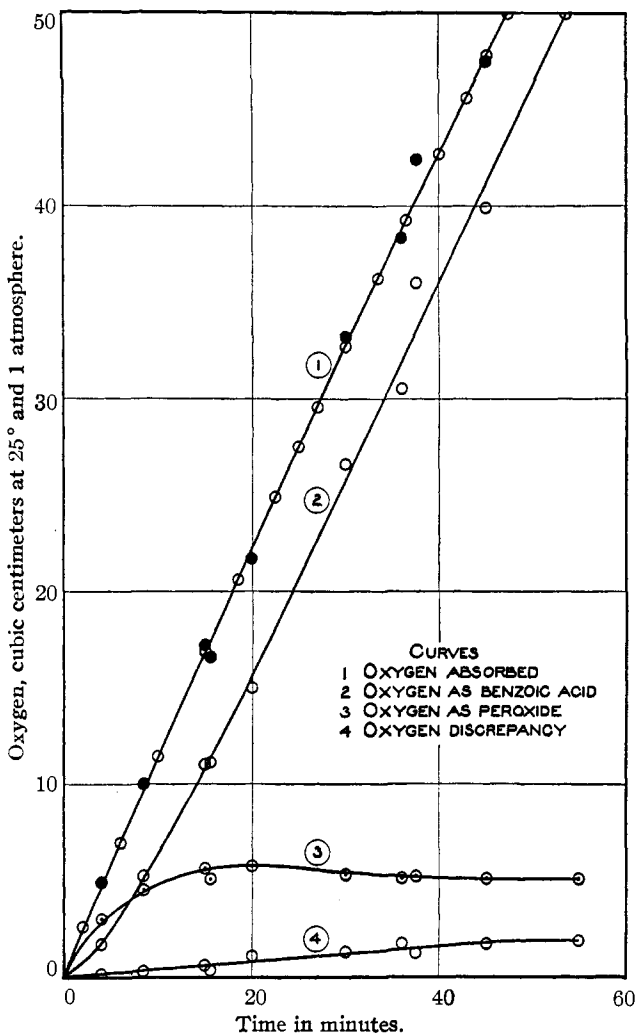


Fig. 3.—Reactions of the benzaldehyde-benzoic acid mixture: curves showing the variation with time of, 1, the total oxygen absorbed, 2, the oxygen used to form benzoic acid, 3, the oxygen in the form of peroxides and 4, the discrepancy between the volume of oxygen absorbed and the oxygen accounted for by analysis.

The rates of formation of benzoic acid at various concentrations of peroxide and benzoic acid are shown in Tables IV and V. A comparison of

TABLE III

DATA ON THE REACTION OF THE BENZALDEHYDE-BENZOIC ACID MIXTURE WITH OXYGEN

Time of reaction, min.	Total absorption, cc.	Oxygen as peroxide, cc.	Oxygen as benzoic acid, cc.	Total oxygen by analysis, cc.	Oxygen discrepancy, cc.
4.00	4.90	3.01	1.72	4.73	0.17
8.42	10.00	4.45	5.25	9.70	.30
15.00	17.20	5.64	11.00	16.64	.56
15.52	16.55	5.08	11.10	16.18	.37
20.00	21.80	5.73	14.95	20.68	1.12
30.00	33.20	5.31	26.60	31.91	1.20
36.00	38.35	5.10	31.55	36.65	1.70
37.60	42.40	5.20	36.01	41.21	1.19
45.02	47.73	5.09	40.92	46.01	1.72
55.10	58.35	5.11	51.40	56.51	1.84

TABLE IV

FORMATION OF BENZOIC ACID IN EXPERIMENTS STARTED WITH BENZALDEHYDE ONLY

Oxygen in the form of peroxides	Oxygen in the form of benzoic acid	Rate of formation of benzoic acid in cc. of oxygen per minute	Rate of formation of benzoic acid divided by the total peroxide concentration
9.0	1.5	0.30	0.33
11.0	2.1	.35	.32
15.6	4.8	.65	.42
16.6	8.0	1.00	.60
16.2	11.5	1.35	.83
15.0	15.6	1.50	1.00
13.6	20.1	1.55	1.14
12.5	23.0	1.55	1.24
10.6	28.8	1.40	1.32
8.9	33.9	1.25	1.40
7.4	38.5	1.10	1.49
6.6	42.6	1.05	1.59
5.9	49.1	1.00	1.69

TABLE V

FORMATION OF BENZOIC ACID IN EXPERIMENTS STARTED WITH THE BENZALDEHYDE-BENZOIC ACID MIXTURE

Oxygen in the form of peroxides	Oxygen in the form of benzoic acid	Rate of formation of benzoic acid in cc. of oxygen per minute	Rate of formation of benzoic acid divided by the total peroxide concentration
3.4	11.6	0.70	2.06
4.5	14.6	.80	1.78
5.0	15.4	.90	1.80
5.5	20.0	.95	1.73
5.7	23.6	1.00	1.75
5.8	25.6	1.02	1.76
5.7	27.7	1.05	1.84
5.6	29.8	1.03	1.84
5.5	31.8	1.02	1.83
5.4	34.9	1.00	1.85



either Figs. 2 and 3 or Tables IV and V shows that the oxidation of benzaldehyde by the peroxides is much faster in the presence than in the absence of benzoic acid, but that only a small amount of the acid is required to obtain the maximum rate. When the autoxidation is started in the absence of benzoic acid the slowness of the formation of benzoic acid permits the accumulation of peroxides over the steady state concentration. This accounts for the marked maximum in curve 3 of Fig. 2. The excess of peroxide, however, is not the original peroxide formed, for, even after sufficient benzoic acid is present, this peroxide is a less effective oxidizer than that formed in the presence of benzoic acid. This is to be seen by comparing the last columns of Tables IV and V, in which the rates of formation of benzoic acid divided by the peroxide concentration are shown. The less reactive peroxide is probably perbenzoic acid, which is formed from another peroxide by a reaction that is inhibited in the presence of benzoic acid. The simplest explanation of this inhibition is that the precursor of perbenzoic acid combines with benzoic acid, forming a compound which readily oxidizes benzaldehyde.

When no benzoic acid is present initially perbenzoic acid is formed and only slowly oxidizes benzaldehyde to benzoic acid which, in turn, inhibits the formation of more perbenzoic acid, the peroxide-benzoic acid compound being formed instead. At the point where the rate of formation of benzoic acid is greatest the ratio between this rate and the peroxide concentration is small because a large fraction of the peroxide is in a less reactive form. As the less reactive peroxide is now being used up faster than it is produced, the peroxides become richer in the peroxide-benzoic acid compound. Hence the values in the last column of Table IV increase, approaching the more constant values of Table V.

When benzoic acid is present initially, very little perbenzoic acid is formed and the peroxides rapidly reach a steady state concentration and a constant composition. This steady state concentration is practically constant when the oxygen pressure is constant and the concentration of benzaldehyde changes only slowly. The change in the concentration of benzaldehyde probably affects the rates of formation and removal of the peroxide in the same way. The values shown in the third and fourth columns of Table V are, consequently, practically constant after the first few minutes.

When benzoic acid is present initially, the rate of absorption of oxygen does not continue to decrease after the first few minutes but the rate is less than the initial rate in the absence of benzoic acid. The peroxide-benzoic acid compound is presumably an inhibitor. This action may be explained if it is assumed that activated benzaldehyde molecules are links in the chain for the absorption of oxygen, and that they can react with the peroxide-benzoic acid complex. The constancy of the rate of absorption of oxygen,

therefore, depends upon the constancy of the steady state concentration of the peroxide-benzoic acid compound. We have ignored the fact that the initial absorption rate is smaller in the presence than in the absence of benzoic acid. This observation is probably not significant, because only after many crystallizations is benzoic acid sufficiently pure that its addition does not produce a distinct induction period, and it is not certain that this influence is entirely absent.

Finally, in the absence of initial benzoic acid, the absorption rate may fall below the constant rate obtained with initial benzoic acid. There is, probably, another reaction path which produces a poison, but which is prevented when a reaction is started in the presence of benzoic acid. It may be seen by comparing the total absorption points of Fig. 3 with those of Fig. 2 that the reactions of the benzaldehyde-benzoic acid mixture were much more reproducible in rate than those started with pure benzaldehyde. This marked difference may be the result of an uncontrolled production of a poison in the latter case. Conditions that favor such a side reaction would rapidly bring the autoxidation to a stop. We have occasionally observed this phenomenon in reactions whose rate at the start was normal but, in a few minutes, decreased below the limits of observation. Rieff<sup>9</sup> shows some similar curves and attributes the phenomenon to extreme dryness. Kuhn and Meyer<sup>10</sup> have obtained inactive benzaldehyde and attribute its inactivity to freedom from traces of catalysts. We did not succeed in obtaining these aborted reactions at will, but we found no such examples in reactions started in the presence of benzoic acid.

### Summary

The distribution of oxygen between peroxides and benzoic acid during its absorption by purified benzaldehyde and by benzaldehyde containing benzoic acid has been quantitatively determined. The reaction is of the first order with respect to oxygen and consists of a series of reactions which involve the formation of peroxides from benzaldehyde and oxygen and the subsequent reaction of these with benzaldehyde to produce benzoic acid.

Certain respects in which the reaction differs from simple, consecutive reactions are due to the autocatalytic nature of the formation of benzoic acid. In the reactions started in the absence of benzoic acid, the peroxides accumulate at first but later their concentration decreases to that of a steady state. In reactions started in the presence of benzoic acid the concentration of peroxides quickly reaches an almost constant value. In both cases the reactions tend to become identical. A mechanism to account for these results has been proposed.

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<sup>9</sup> Rieff, *THIS JOURNAL*, **48**, 2893 (1926).

<sup>10</sup> Kuhn and Meyer, *Naturwissenschaften*, **16**, 1028 (1928).