

Temperature, °C.	500	450	360	380	380
Init. press. N <sub>2</sub> H <sub>4</sub> , mm.	7.5	9.5	8	9	9
Init. press. H <sub>2</sub> , mm.	...	...	8	...	14
Tot. press. incr., %	93	106	98	91	93

The measurement of the temperatures of filaments in the manner described above is not particularly accurate, but it is clear that at temperatures approximately close to each other hydrazine decomposes on tungsten and platinum in a manner quite different from that which it follows on quartz, but similar to that which obtains in the presence of excited mercury and on illumination. For this singular behavior on quartz we can at present offer no explanation. It might be pointed out that the discrepancy between the pressures used in the quartz and filament reactions is of no significance, because Elgin, when he first noticed the reaction on quartz, was using pressures of 8 to 10 mm.

In conclusion, we should like to state that we have been enabled to carry out this work thanks to a Procter Visiting Fellowship at Princeton. We should also like to express our appreciation of the advice and helpful suggestions we have received from Professor Hugh S. Taylor.

### Summary

The thermal decomposition of hydrazine on quartz and also on platinum and tungsten wires has been studied. On quartz the reaction follows the course  $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2$ , while on platinum or tungsten it follows the course  $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ .

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

## THE OXIDATION OF BENZALDEHYDE AND FORMALDEHYDE IN THE GASEOUS PHASE

BY PHILIP J. ASKEY

RECEIVED NOVEMBER 8, 1929

PUBLISHED MARCH 6, 1930

Recently it has been observed that a number of oxidations in the gaseous phase appear to be chain reactions. This is true of the vapor-phase oxidations of phosphorus,<sup>1</sup> of the homogeneous reaction of hydrogen and oxygen,<sup>2</sup> of the oxidation of propane and the butanes,<sup>3</sup> and of several other reactions. The chief characteristic of such reactions is the suppression of the rate of oxidation when the reaction vessel is packed with material of the same nature as itself, and this inhibiting effect is enhanced when the quartz or glass packing is coated with some inert substance like potassium chloride.

<sup>1</sup> Semenoff, *Z. Physik*, **46**, 109 (1927).

<sup>2</sup> Hinshelwood, *Proc. Roy. Soc. London*, **118A**, 170 (1928).

<sup>3</sup> Pease, *THIS JOURNAL*, **51**, 1839 (1929).

At the same time, several oxidation reactions in the liquid phase, both thermal and photochemical, have been shown to be chain reactions.<sup>4</sup> The work of Engler, Bach and others had indicated that in a number of autoxidation processes there is intermediate formation of peroxide bodies which then react further with the original substance, and in his investigation of the liquid phase oxidation of benzaldehyde, Bäckström<sup>4b</sup> demonstrated conclusively that benzoperacid was an intermediate product and subsequently reacted with further aldehyde. In addition to this he showed that it was the reaction resulting in the formation of the benzo-peracid which gave rise to the activation necessary for the continuity of the chain. From work that has been done by Gill, Mardles and Tett<sup>5</sup> and by Pope, Dykstra and Edgar,<sup>6</sup> as well as by Pease,<sup>3</sup> it appears not only that aldehydes are intermediate products in the oxidation of various hydrocarbons, but also that they exhibit, when oxidized themselves, characteristics such as luminescence and sensitiveness to inhibition which are typical of chain reactions. Pease, therefore, concludes that the aldehyde oxidation is the basis of his chain mechanism for the oxidation of hydrocarbons. It should, however, be pointed out that Gill, Mardles and Tett<sup>5</sup> in studying the oxidation of hexane, came to the conclusion that the luminescence was due not to the intermediate formation of aldehydes but to the formation of primary peroxides of hexane.

In this paper we wish to present the results of a few preliminary experiments on the oxidation of benzaldehyde and formaldehyde in the vapor state. These experiments, while they do not provide a detailed and intimate picture of the mechanism of the oxidation process, at least indicate a few significant features. In the first place, they indicate that both oxidation processes are chain reactions, characterized by a considerable suppression of the rate when the reaction bulb is packed with quartz; secondly, that in the case of benzaldehyde, oxygen itself acts as an inhibitor when present in excess. There also appears evidence that there is a slight induction period in the oxidation of benzaldehyde, while none was apparent in the oxidation of formaldehyde.

The oxidation of benzaldehyde proceeds at about 200°; that of formaldehyde at about 330°.

### Experimental Method

The method used was the same for both benzaldehyde and formaldehyde. The oxidation was carried out in a quartz bulb of about 200-cc. capacity heated in an electric furnace, the temperature of which was measured by means of a thermocouple. All the external connections of the apparatus

<sup>4</sup> (a) Bäckström, *THIS JOURNAL*, **49**, 460 (1927); (b) *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 15; (c) **6**, No. 16.

<sup>5</sup> Gill, Mardles and Tett, *Trans. Faraday Soc.*, **24**, 575 (1928).

<sup>6</sup> Pope, Dykstra and Edgar, *THIS JOURNAL*, **51**, 1875 (1929).

were wound with nichrome wire and maintained at about 100°. Stop-cocks were dispensed with and mercury operated valves, which could be heated to 100°, were substituted.

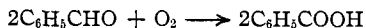
Freshly distilled benzaldehyde or paraformaldehyde was contained in small bulbs sealed onto the apparatus, and the required pressure of aldehyde was obtained by heating the bulb. It was then shut off from the reaction vessel. Oxygen was admitted from a gas holder and the course of the reaction was followed by the pressure change indicated by a constant volume manometer.

For the reactions in a packed bulb the latter was filled with coarse quartz grains which had been carefully cleaned with nitric acid, washed and dried.

In one or two experiments with benzaldehyde a rough attempt was made to analyze some of the products of reaction. These were withdrawn into a gas holder through a U-tube cooled in solid carbon dioxide and ether. This, presumably, condensed out all but carbon dioxide, carbon monoxide and permanent gases. The residue was then passed through liquid air to remove any carbon dioxide, and the diminution of pressure was noted. The fraction condensed out with solid carbon dioxide and ether was distilled into another vessel and examined, but the quantity of material was so minute that little information could be obtained.

### Discussion of Results

(1) **Benzaldehyde.**—A series of experiments was carried out at a temperature of 198° with different initial pressures of benzaldehyde and oxygen. It has been assumed that the final product of the oxidation would be benzoic acid



and that there would be a final decrease in pressure equal to half the initial pressure of benzaldehyde. It was found that this was only true when the initial pressure of oxygen was almost double that required by the above equation. When the proportion of oxygen was less than this, the reaction, although it went at a greater rate than when more oxygen was present, stopped short at a point which would have appeared to indicate incomplete oxidation. We shall return to the explanation of this later. In every reaction there was a final increase of pressure of one or two millimeters; due possibly to a slow decomposition of the products.

In the following table are given the final pressure decrease and the times taken to reach this pressure by mixtures of benzaldehyde and oxygen in different proportions.

TEMPERATURE, 198°C.							
Initial pressures, mm.	{	Benzaldehyde	38	30	33	30	23
		Oxygen	24	20	21	28	32
Final pressure decrease, mm.			12.5	10	10	13	10.5
Time to reach final press. decr., min.			18	16	32	91	91

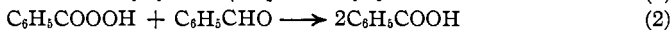
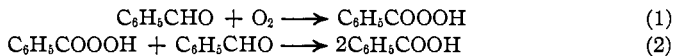
By "final pressure decrease" we mean the maximum pressure decrease reached before the subsequently slow and comparatively small pressure increase.

The following table shows the difference in the rate of oxidation in an empty bulb and a packed bulb.

Bulb	Temp., °C.	Initial pressure, mm.		Time taken to reach x % of final pressure decrease, minutes										
		Benz- aldehyde	Oxy- gen	10	20	30	40	50	60	70	80	90	100	
Empty	198	38	24					13						
Empty	198	23	32	8	16	21		36			55			91
Empty	198	30	20	3		5		7		10				16
Empty	198	33	21		4.5			11		14	19			32
Empty	198	30	28		14			34			54			81
Packed	198	34.5	25			300			1440					5760
Packed	198	35	47					Very slow						
Empty	224	30.5	26			1				4				7
Packed	224	30.5	24.5	120										800
Empty	242	36	85					Very slow						

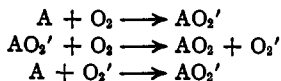
A complete investigation should, of course, include the influence of other gases on the reaction, and also the result of a wider variation of the initial pressures of benzaldehyde and oxygen. It is, however, quite clear that the oxidation of benzaldehyde exhibits the main characteristics of a chain reaction—the suppression of the rate in a packed bulb. The above experiments also show the inhibiting effect of excess oxygen, and in this respect parallel the observations of Pease on the oxidation of propane and the butanes.

The mechanism of the chain propagation is still somewhat of a moot point, although it seems most likely, by analogy with other oxidations and particularly that of benzaldehyde in the liquid phase, that benzo-peracid is the first product of oxidation, subsequently reacting with a further molecule of benzaldehyde



The question then arises as to which of these reactions is responsible for the activation of another molecule of benzaldehyde and the continuance of the chain. In the liquid-phase oxidation, Bäckström showed that it was the first reaction which was primarily responsible for further activation. At the same time he showed that there is no reason why the reaction between the peracid and aldehyde should not cause activation of other molecules, but to a much smaller extent, which would then react both with oxygen and with benzoperacid. This makes the benzaldehyde the active principle in chain propagation.

An alternative view is that the oxygen is the reactant activated by collision, the oxygen acting as a promoter of the chain



but if we compare the reaction rate for a mixture of 30 mm. of benzaldehyde and 20 mm. of oxygen with that for a mixture of 23 mm. and 32 mm., respectively, it seems fairly clear that it must be the benzaldehyde which is promoting the chain, while the oxygen acts as an inhibitor by breaking the chain in the same way as collision with the wall breaks it, *i. e.*, by taking up the energy of activation, and acting as a carrier of this energy to the wall. Moreover, the former mechanism more readily explains the autocatalytic effect which is observed in this and other oxidations and which is illustrated by the following data.

TEMPERATURE 198°

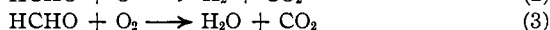
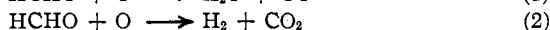
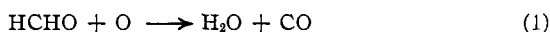
(1) Initial pressures: benzaldehyde, 23 mm.; oxygen, 32 mm.					
Time, minutes	0	3	8	15	20
Pressure decrease, mm.	0	0	1	2	3
(2) Initial pressures: benzaldehyde, 30 mm.; oxygen, 28 mm.					
Time, minutes	0	2	10	20	30
Pressure decrease, mm.	0	0	1.2	8.2	5.3

We may return now to the fact stated above, that in reactions involving smaller proportions of oxygen, the oxidation, although proceeding at a faster rate, did not give the final pressure increase corresponding to complete oxidation to benzoic acid. In one or two experiments the gaseous products were analyzed for carbon dioxide as described above. It was observed that in the reactions involving a high proportion of oxygen there was practically no carbon dioxide formed; but that in those involving a lower proportion of oxygen, carbon dioxide was present in amount approximately equal to the apparent deficiency of oxidation. Thus in the reaction in which the initial pressures of benzaldehyde and oxygen were 33 mm. and 21 mm., respectively, and in which the maximum pressure decrease was 10 mm., there was approximately 6 mm. of carbon dioxide; while in a reaction in which the initial pressures were 30 mm. and 28 mm., respectively, and the maximum pressure decrease was 13 mm., there was only about 2 mm. of carbon dioxide. It was thought that possibly in the reaction involving a smaller proportion of oxygen some of the benzoic acid decomposed to phenol and carbon dioxide, but an attempt to detect phenol in the products of reaction was unsuccessful. Moreover, Erlenmeyer<sup>7</sup> showed that benzoic acid on heating yielded only minute traces of carbon dioxide, decomposing instead to benzoic acid and oxygen. A possible alternative is that the carbon dioxide arises from decomposition of the benzoic acid in an activated state.

<sup>7</sup> Erlenmeyer, *Helv. Chim. Acta*, 10, 620 (1927).

The temperature coefficient of the reaction as it stands is fairly high; but this is no measure of the temperature coefficient of the simple bimolecular reaction between benzaldehyde and oxygen. This might possibly be measured in two ways: (1) in the presence of excess oxygen, or (2) in a bulb packed with very fine silica and at low pressures. In either method it is conceivable that the chains would be broken as soon as they were started, and only the primary reactions would have effect.

(2) **Oxidation of Formaldehyde.**—There are three possibilities for the oxidation of formaldehyde



The pressure increase corresponding to Reactions 1 and 2 would be half the initial pressure of formaldehyde, while (3) would show no change. In the temperature range 320 to 340°, the final pressure increase was not far short of the value corresponding to (1) or (2), but at higher temperatures the pressure increase became less and at 380° was only about one-half the value given by (1) or (2). It seems that either (1) or (2) and (3) can occur simultaneously, (3) having the higher temperature coefficient. Gas analyses to distinguish between (1) and (2) were not made.

A few reactions were carried out to determine whether the reaction was suppressed when carried out in a packed bulb, and the results are given in the following table.

Bulb	Temp., °C.	Initial press., mm.		Time for x % reaction, minutes								
		HCHO	O <sub>2</sub>	10	20	30	40	50	60	70	80	
Empty	321	48	40	3		10		36				
Empty	321	41	22					23				
Packed	321	49	45		350			1380				
Packed	321	53	59		600		1500					
Empty	346	47	36.5	1				1	5	10	15	36
Empty	346	48	38					5	5	9	17	36
Packed	346	44	40		240	480						

In the next table is shown the variation of the final pressure increase with temperature.

Temperature, °C.		321	346	370	370	400
Initial press., mm.	HCHO	44	48	48	42.5	47.5
	O <sub>2</sub>	40	38	63	36	47
Final press., mm.		20.5	22	12.8	10	6 (approx.)

These experiments are far from exhaustive, but they indicate that the oxidation of formaldehyde has a chain mechanism similar to that discussed in the previous part of the paper.

In conclusion we should like to express our appreciation of the very kind and helpful suggestions we have received from Professor Hugh S.

Taylor, from Dr. Hans L. J. Bäckström and from Dr. R. N. Pease. We should also like to state that we are indebted to a Procter Visiting Fellowship at Princeton for assistance in carrying out this work.

### Summary

The thermal oxidations of benzaldehyde and formaldehyde in the vapor phase have been investigated. It has been shown that they are both chain reactions, judged by the characteristic suppression of the rate of oxidation when it is carried out in a packed vessel. The mechanism of the benzaldehyde oxidation is discussed.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTH CAROLINA FOOD RESEARCH COMMISSION AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

## THE DETERMINATION OF TRACES OF IODINE. IV. IODINE IN SMALL QUANTITIES OF THYROID AND OTHER TISSUES<sup>1</sup>

BY ROE E. REMINGTON, J. F. MCCLENDON, HARRY VON KOLNITZ AND F. BARTOW CULP

RECEIVED NOVEMBER 25, 1929

PUBLISHED MARCH 6, 1930

The tube furnace method originated by one of us<sup>2</sup> for the destruction of organic matter in the estimation of traces of iodine has been modified and adapted to the analysis of thyroid and other glands, oysters and other animal tissues relatively high in iodine. It possesses advantages of brevity and accuracy which make it preferable to any other method which has been described. Other workers have destroyed organic matter in thyroid by fusion with sodium hydroxide, or with sodium hydroxide and potassium nitrate<sup>3</sup> or a carbonate mixture. It has also been done by digestion with sulfuric acid and hydrogen peroxide.<sup>4</sup> All of these processes are time consuming and open to the possibility of loss.

We have found<sup>5</sup> that vegetables can be ignited in a muffle at 450° or less without material loss of iodine but if the temperature is raised to 550° the results are usually low. On dried thyroids, alone or with the addition of calcium oxide or sodium hydroxide, the low-temperature method is not satisfactory. If 0.1 g. of dried thyroid is mixed with 100 g. of dried potatoes, the iodine can be recovered with a fair degree of accuracy, but requires from twelve to twenty-four hours in the muffle and previous careful analysis of the potatoes.

<sup>1</sup> Presented before the Division of Biological Chemistry at the 78th meeting of the American Chemical Society, Minneapolis, Minnesota, September 9-13, 1929.

<sup>2</sup> J. F. McClendon, *THIS JOURNAL*, **50**, 1093 (1928).

<sup>3</sup> E. C. Kendall, *J. Biol. Chem.*, **43**, 149 (1920).

<sup>4</sup> G. Pfeiffer, *Biochem. Z.*, **195**, 128 (1928); E. Glimm and J. Isenbruch, *ibid.*, **207**, 368 (1929).

<sup>5</sup> J. F. McClendon and R. E. Remington, *THIS JOURNAL*, **51**, 395 (1929).