TIN VANADATE AS A CATALYST IN THE OXIDATION OF TOLUENE TO BENZOIC ACID[1]

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INTRODUCTION

It has been known for centuries that certain gums are capable of preventing decay. Some of these gums were used by the Egyptians in the preservation of their dead. It was found that the preserving action of these gums was due to benzoic acid, one of their constituents. The insects caught by some insectiverous plants are preserved for long periods of time by the benzoic acid excreted from the leaves of these plants. At the present time use is made of the preserving action of this acid and its salts in the treatment of certain foods to prevent spoilage. The acid and its salts also find some use in medicine as well as in the manufacture of certain dyes.

When the acid or its salt is to be used in medicine or for the preservation of foods, the presence of certain impurities is considered to be particularly harmful. Much of the acid produced from chlorinated toluene contains combined chlorine as an impurity. Since the removal of this material presents a difficult problem, some other method for preparing benzoic acid from toluene is being sought.

In 1875 Coquillion (2) found that toluene vapor could be oxidized to benzoic acid by air in the presence of certain catalysts. Weiss and Downs (7) have given a review of the literature on the subject of catalytic oxidations, along with a report concerning their own work in this field. One of the most outstanding researches on the catalytic oxidation of toluene is that of Maxted (6) in which he used a catalyst of tin vanadate.

Advantages of a vapor phase catalytic process for the preparation of benzoic acid from toluene are obvious. The product may be made to sublime from the reaction chamber in a comparatively pure state with no inorganic contamination. Air has a sufficiently high concentration of oxygen to bring about the desired reaction, providing other conditions are properly chosen. Since the reaction is exothermic, external heating of the

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[1] This paper is based upon a thesis submitted to the Graduate School of Indiana University by Roy Huitema in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1934.

apparatus should be unnecessary. Any by-products of the catalytic process for the oxidation of toluene should be of such a nature as to present no difficulty in their disposal.

Numerous patents have been granted covering the use of certain materials as the contact mass in the vapor phase catalytic oxidation of toluene and related compounds. The catalysts which find the greatest favor with the investigators are the compounds of vanadium. In fact many oxidations, both organic and inorganic, are catalyzed by compounds of this element. Although vanadium pentoxide was one of the compounds first used in this type of work, it has been supplanted to some degree by the vanadates. Since tin vanadate has been reported to be especially active in the oxidation of toluene to benzoic acid, it was thought advisable to investigate the behavior of this catalyst a little more closely.

THEORETICAL CONSIDERATIONS

Several possible reactions may take place in the oxidation of such a compound as toluene. The nature of the reactions and the extent to which they occur are determined largely by the following conditions: temperature of the reaction chamber, pressure, nature of the catalyst, nature and proportion of diluent gases, and the proportion of oxygen to toluene vapor.

From a technical point of view the question of greatest importance is that concerning the ratio of the quantity of toluene converted to the desired product to the total amount of toluene consumed in the process. The reaction, too, must be of such a nature as to proceed with a sufficiently high velocity to be profitable.

A number of non-reactive vapors or gases have been suggested for use as diluents for the air used in vapor phase oxidation. It may be that in some cases a diluent tends to blanket side reactions which take place. Other diluents merely decrease the concentration of one or more of the reactants and thereby lessen the speed of the reaction.

Water vapor added to the reacting gases may serve as a means of carrying some of the less volatile products from the reaction chamber. However, if water is a product of the desired reaction, its addition may have a detrimental effect. The addition of any vapor or gas to the reactants increases the velocity with which they pass over the catalyst surface and therefore decreases the time of contact.

Perhaps the greatest benefit of the addition of inert materials to the reaction mixture is the tendency of these materials to maintain a more uniform temperature of the catalyst by absorbing some of the heat liberated in the reaction. If the reaction takes place at points on the surface of the catalyst, the heat liberated at these points may raise their temperature to such an extent that the products of the reaction will be different from those which would have been obtained had the temperature been held constant. Investigators (8) using glass apparatus report that when air and toluene vapor are mixed and passed over a catalyst heated to a temperature of from 200 to 300°C., points on the surface of the catalyst are heated to redness by the heat liberated in the reaction.

The following thermal equations show that a large quantity of heat will be liberated when the desired reaction takes place.

$$C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O + 935.6 \text{ kg-cal.[2]} \qquad (1)$$

$$C_6H_5COOH + 7.5O_2 \rightarrow 7CO_2 + 3H_2O + 771.2 \text{ kg-cal. (3)} \qquad (2)$$

By subtracting equation 2 from equation 1 we get the following equation:

$$C_6H_5CH_3 + \tfrac{3}{2}O_2 \rightarrow C_6H_5COOH + H_2O + 164.8 \text{ kg-cal.} \qquad (3)$$

If one molecular weight of toluene is completely oxidized, there are 935.6 kg-cal. of heat liberated. Nine molecular weights of oxygen will be consumed in the process. However, if nine molecular weights of oxygen are utilized to oxidize toluene to benzoic acid, there will be 6 × 164.4 kg-cal. of heat liberated. This amounts to 50.8 kg-cal. more than the amount liberated when this same weight of oxygen is consumed in the complete oxidation of toluene.

The temperature at which a particular reaction may be catalyzed is dependent upon the catalyst used. For example, if a mixture of air and toluene vapor is passed over a vanadium pentoxide catalyst, the temperature must be nearly 400°C. before an appreciable amount of benzoic acid is formed. If some other catalyst is used, this same mixture will react at a different temperature.

EXPERIMENTAL PROCEDURE

The work herein reported was done in an attempt to determine the applicability of a tin vanadate catalyst to the vapor phase oxidation of toluene to benzoic acid. The effect of preliminary heating upon the activity of tin vanadate and the effects of such variables as reaction temperature, concentration of oxygen, and the addition of diluent gases were studied. Not only was the percentage of toluene converted to benzoic acid determined, but also a measure was taken of the extent to which the toluene was completely oxidized.

The apparatus consisted of a reaction chamber of black iron 3 in. long and 1½ in. in diameter fitted at the bottom end with a cap and at the top with a reducer, T. The lower cap was drilled and threaded to take a ½-in. pipe through which the gases might enter the reaction chamber. The gases passed up through the catalyst and out of the chamber through the

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[2] This is the average of the values given by Kharasch (5).

side arm of the T. The upper opening of the T was bushed down to take a $\frac{1}{4}$-in. pipe which extended down to the top of the catalyst. This last named pipe was capped at the lower end and carried a copper-advance thermocouple for measuring the temperature of the gases as they came from the catalyst. Since the position of maximum temperature in the body of a catalyst varies from time to time and is dependent upon the age of the catalyst, rate of gas flow, and other conditions, the temperature of the gas coming from the catalyst was taken as the working temperature of the catalyst. A diagram of the apparatus used is shown in figure 1.

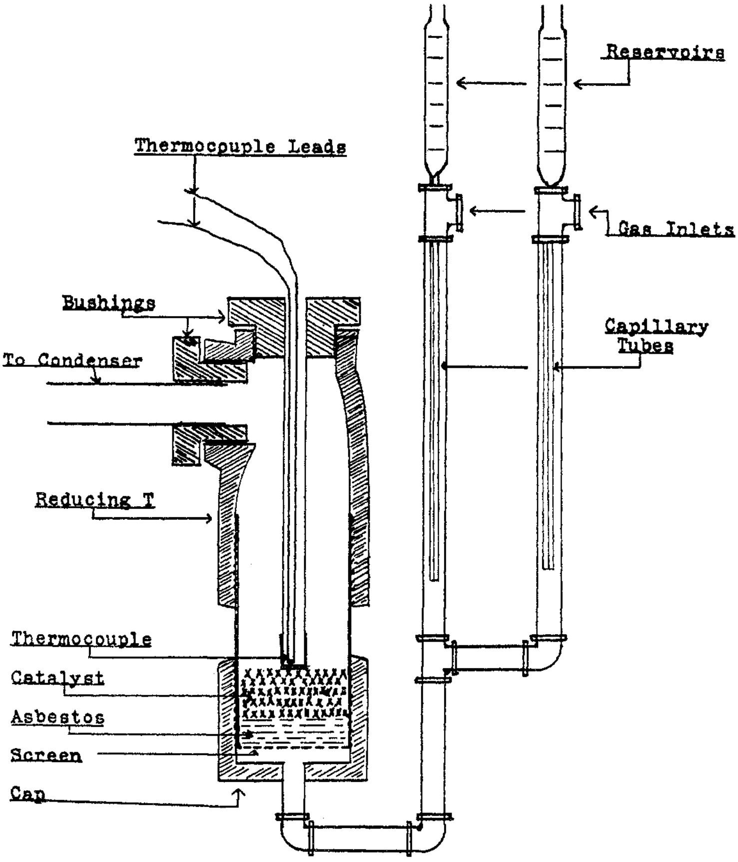

FIG. 1. Diagram of the apparatus (approximately two-thirds actual size)

The entire apparatus with the exception of the reservoirs and the condenser was placed in a tin can 8¼ in. tall and 6½ in. in diameter on the inside of which 30 ft. of No. 16 B. and S. gauge chromel wire was imbedded in alundum cement. The chromel wire acted as the heating unit and was placed in series with an outside resistance. After the apparatus was placed in the can in the desired position the remainder of the can was filled with sand. This was done so that all parts of the apparatus would be held at a uniform temperature. The variation in temperature of the gases coming from the catalyst never amounted to more than 2°C. for a given run.

Toluene was placed in the reservoir by means of a calibrated pipet and forced into the furnace at the desired rate through the connecting capillary. Since the capillary tube was heated to a temperature well above the boiling point of toluene, this material was vaporized before it reached the bottom end of this tube. At this point the vapor came in contact with the incoming air. Ample mixing of the vapor with the air took place as the two materials passed through the iron tube leading to the catalyst chamber and in their passage through the asbestos catalyst support. The desired rate of toluene flow was obtained by means of mercury leveling bulbs which regulated the pressure on the surface of the toluene in the reservoirs.

The gas flow into the furnace was kept constant throughout the run and for 90 minutes after the last of the toluene had entered the furnace. This was done in order that the greater portion of the benzoic acid which had been formed would be carried from the furnace.

In all of the work to be reported here 2 cc. of toluene (1.707 g.) was fed into the furnace in thirty minutes. After the washing period was finished the benzoic acid which had been formed was washed from the condenser with alcohol and water.

Any carbon dioxide which remained in the solution washed from the condenser was removed before the benzoic acid was titrated. This was done by bubbling carbon dioxide-free air through the solution for forty minutes. The acid was then titrated with $N/10$ sodium hydroxide solution which had been standardized against C.P. benzoic acid. Phenolphthalein was used as indicator.

The first run made under a given set of conditions was discarded; data were collected from subsequent runs. The 90-min. wash period was not sufficient to remove all of the benzoic acid from the furnace, but it was considered reasonable to assume that the amount of acid which was carried over from one run to the next would be constant. Any inaccuracy due to this carry-over from one run to the next was less than the inaccuracies due to errors which might develop from other sources.

The escaping gas from the condenser was passed through concentrated sulfuric acid to remove the vapors of water and toluene. Next, it passed through two weighed tubes of potassium hydroxide solution (sp. gr. 1.27), and finally through a weighed tube of concentrated sulfuric acid with a glass wool filter on the end. The difference in the sum of the weights of the potassium hydroxide tubes and the weighed sulfuric acid tube before and after the run was taken as the weight of the carbon dioxide produced. The removal train was connected to the condenser during the time toluene was being fed into the furnace and for five minutes after the last of the toluene had entered the furnace. The weight of carbon dioxide found in this manner was not entirely accurate, but the method served as a means of determining the relative losses of starting material.

The back pressure created by the carbon dioxide removal train was relieved by means of an aspirator. In this way it was possible to keep the pressure within the reaction chamber equal to that of the atmosphere.

The tin vanadate used as catalyst in this work was prepared by precipitation. A hot solution of carefully purified ammonium metavanadate was added to a dilute solution of stannic chloride (sp. gr. 1.075) to precipitate the tin vanadate. The product was washed several times by decantation. It was then filtered on a Büchner funnel and washed until the filtrate was practically free of chlorides.

When the washing was completed, the material was transferred to a large evaporating dish and dried for thirty-six hours at 110°C. The drying process was hastened by breaking up the lumps and by stirring the material occasionally. The dried tin vanadate was a rather hard, brittle material and was chocolate colored. It was broken up by means of a mortar and pestle until it would pass through a 20-mesh sieve.

The tin vanadate prepared as described above was divided into three parts, one of which was used directly as the contact mass in the oxidation of toluene to benzoic acid. This unheated material will be spoken of as catalyst A. Another portion of the material was placed in a cold muffle furnace and slowly heated to 400°C., maintained at that temperature for thirty minutes, and then allowed to cool. Tin vanadate treated in this manner will be spoken of as catalyst B. The third portion of the untreated material was heated in a furnace at 700°C. for thirty minutes. This material will be called catalyst C. When the temperature of the furnace in which catalyst C was being heated reached 450°C., some ammonium chloride was expelled from the material. The heated catalysts took on a yellowish color.

The apparent volume of catalyst used in each case was 30 cc. The material was spread evenly over the asbestos base, so that the reacting gases would pass through equal thicknesses of the contact mass.

Before any data were taken the catalysts were used for several days in the oxidation of toluene so that they would reach a constant degree of activity. This precaution was apparently unnecessary, as there was little or no change in the activity noticed after a few runs had been made.

RESULTS

The data in table 1 are made up of the results of a series of runs carried out in an attempt to determine the temperature at which the conversion of toluene to benzoic acid would be most practical. These data are represented graphically in figures 2 and 3. It is apparent that the temperature at which the highest percentage of toluene is converted to benzoic acid is 243°C., and that the percentage of toluene completely oxidized increases rapidly with increasing temperature.

On comparing the different catalysts, it is seen that the heating of tin vanadate changes its nature to a considerable extent. The exact nature of this change has not been determined, but it may be due to the driving off of occluded ammonium chloride. It is possible, too, that a change in crystalline structure took place during the heating period. Appreciable sintering of tin vanadate takes place at a little higher temperature than that to which catalyst C was heated.

TABLE 1

Determination of most practical temperature for the conversion of toluene to benzoic acid

Air flow: 7 liters per hour, which represents 100 per cent of the amount of oxygen required to oxidize the toluene to benzoic acid. Toluene flow: 3.414 gm. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C.	PER CENT TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
210	8.50	6.45	3.83	5.51	5.95	2.64
221	9.72	8.59	5.25	11.02	11.42	3.73
228	10.55	9.55	7.90	14.10	13.79	8.45
243	11.00	9.75	11.90	19.80	17.93	20.62
246	9.80	9.29	9.80	22.82		
261	7.17	7.85	7.17	25.42	19.48	21.60
270	6.45	7.61	6.45	27.43	22.70	21.70

In order to ascertain the effect of oxygen concentration upon the amount of toluene converted to benzoic acid and upon the amount of toluene completely oxidized, a series of runs were made using different rates of air flow. The temperature chosen for these runs was 236°C. At this temperature the conversion of toluene to benzoic acid was of the same order for all three catalysts, and there was no danger of exceeding the optimum operating temperature of any of them. The results of this series of runs are shown in table 2.

The data in table 2 indicate the effect of variation of oxygen concentration upon the percentage of toluene changed to benzoic acid and upon the percentage of toluene completely oxidized. The data show clearly that even though the percentage of toluene converted into benzoic acid is somewhat higher at the higher oxygen concentrations, the loss of toluene as carbon dioxide and water is very much greater at these concentrations. In the production of benzaldehyde from toluene by the use of air as the oxidizing agent in the presence of a vanadium pentoxide catalyst, Green (4) states that equimolecular quantities of oxygen and toluene vapor give good results and that Gibbs has indicated that two and one-half times that concentration is desirable. The data in table 2 show plainly that even lower oxygen concentrations are desirable in the production of benzoic acid from toluene by the use of a tin vanadate catalyst. The great change in the amount of carbon dioxide produced with changing oxygen concentrations makes it apparent that a delicate means of control for the air flow is essential in this type of work. A graphical representation of the effect of oxygen concentration upon the percentage of toluene converted to benzoic acid is given in figure 4.

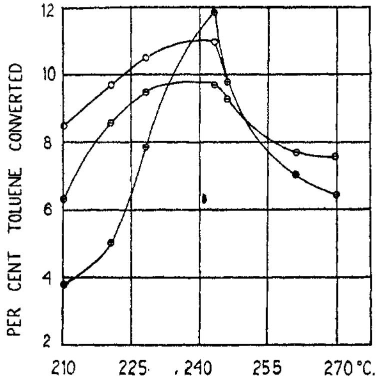

FIG. 2. The effect of temperature upon the per cent of toluene converted to benzoic acid. ○, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

TABLE 2

The effect of oxygen concentration

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT OF TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
50	8.57	8.04	6.05	11.05	9.95	4.18
71.5	8.66	8.43	6.13	11.31	11.32	4.54
100	9.29	9.47	9.47	19.37	16.05	11.91
143	9.15	10.12	11.10	20.95	20.59	18.92

A relative measure of the amount of toluene consumed per pass which was converted to benzoic acid is given in the data in tables 3 and 4. The data in these tables were compiled by adding the per cent of toluene converted to benzoic acid to the per cent lost by complete oxidation. The per cent converted to benzoic acid was divided by this sum; the quotient obtained in this manner was then multiplied by 100. This final value shall be called the conversion ratio.

The data in table 3 show the effect of temperature upon the conversion ratio. Since there may have been some error in the carbon dioxide determination the values given are only relative. These data show that the conversion ratios for all three catalysts decrease with increasing temperature. Although the ratio for catalyst B is lower than the ratios of the other two catalysts at the lower temperatures, it is higher than the other ratios at the higher temperatures. The values of the different ratios were almost the same at the temperature at which the greatest percentage of toluene was converted to benzoic acid per pass (243°C.).

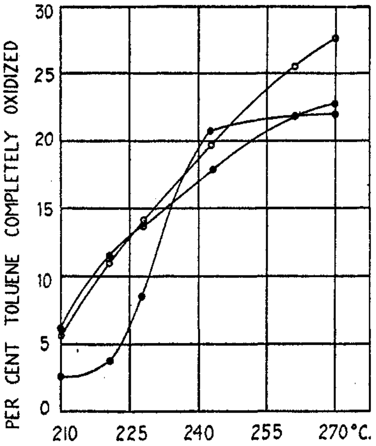

FIG. 3

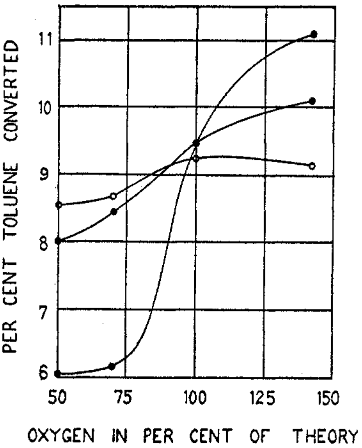

FIG. 4

FIG. 3. The effect of temperature upon the per cent of toluene completely oxidized. ○, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

FIG. 4. The effect of oxygen concentration upon the per cent of toluene converted to benzoic acid. ○, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

The data in table 4 show the effect of oxygen concentration upon the conversion ratios of the different catalysts studied. It is shown by these data that the higher the oxygen concentration the higher the losses of toluene by complete oxidation. At the temperature chosen the conversion ratio for catalyst C is consistently higher than the ratios of the other two catalysts.

The variations of conversion ratios from one catalyst to another indicate that there is an essential change brought about in the catalytic activity of tin vanadate by preliminary heating. These differences suggest the possibility of finding a catalyst which under the proper conditions would convert a greater portion of the toluene consumed to benzoic acid. Had this ratio been the same for all of the catalysts under the same set of conditions, the prospects for finding a better catalyst would have been small. It may be possible to find some foreign substance which when added to tin vanadate will blanket the reaction in which carbon dioxide is formed and thus produce a higher conversion ratio. This assumption is substantiated by the work of Charlot (1) in which he used various catalysts in the oxidation of toluene and its derivatives and found that there was a close relation between the extent of complete oxidation and the catalyst used. This relation was different for different catalysts, but it was essentially the same for a given catalyst irrespective of the compound oxidized.

TABLE 3

The effect of temperature upon the conversion ratio

Air flow: 7 liters per hour (100 per cent of the amount necessary to oxidize all of the toluene to benzoic acid). Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C.	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED TO BENZOIC ACID USING CATALYSTS		
	A	B	C
210	60.7	52.1	59.1
221	46.9	42.9	58.4
228	42.8	40.8	48.2
243	35.7	35.2	36.6
261	22.4	28.7	25.0
270	18.7	25.2	23.8

TABLE 4

The effect of oxygen concentration upon the conversion ratios of the catalysts

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED INTO BENZOIC ACID USING CATALYSTS		
	A	B	C
50.0	44.5	44.7	59.0
71.5	43.5	42.6	57.5
100.0	32.4	37.1	44.3
143	30.4	33.1	37.0

In order to determine whether or not the addition of carbon dioxide to the reacting gases would produce a higher percentage of benzoic acid from toluene, a series of runs was made in which carbon dioxide was added to the mixture of air and toluene vapor. The results of this series of runs are shown in table 5.

The data in table 5 indicate that the addition of carbon dioxide to the reacting gases has no beneficial effect,—at least there is no increase in the amount of benzoic acid produced per pass. Since no measure was taken of the extent of complete oxidation, we are not in a position to say definitely how the presence of carbon dioxide affected the conversion ratio, but in view of the other work which has been done on this subject, it is likely that the conversion ratio was not affected to any great extent. The decrease in the benzoic acid yield was probably due to the increased velocity of gas over the catalyst. A run was made with an air velocity of 3.5 l. per hour and with the same velocity of carbon dioxide. The oxygen concentration in this case was 50 per cent of the theoretical amount required to oxidize the toluene to benzoic acid, while the total gas velocity was essentially the same as when the oxygen concentration was 100 per cent and no carbon dioxide was added. The benzoic acid produced under these conditions was the same as when none of the diluent was added.

TABLE 5

Runs made in which carbon dioxide was added to the mixture of air and toluene vapor

Catalyst: tin vanadate heated to 400°C. Temperature, 236°C. Air flow: 7 l. per hour (100 per cent theoretical oxygen)

CARBON DIOXIDE ADDED IN LITERS PER HOUR	PER CENT TOLUENE CONVERTED TO BENZOIC ACID
None	10.67
5	8.91
10	7.26

When water vapor was added to the reacting gases, the extent of complete oxidation was the same as when no water vapor was added, and the benzoic acid yield was appreciably decreased.

In all of the work herein reported small quantities of anthraquinone and benzaldehyde were formed. Although no measure was taken of these quantities, the anthraquinone production appeared to increase with increasing temperature and also with the addition of carbon dioxide to the reaction mixture.

CONCLUSIONS

1. Tin vanadate is an excellent catalyst for the oxidation of toluene to benzoic acid.
2. Heating previous to use has a marked effect upon the behavior of tin vanadate as a catalyst in the reaction studied.

3. The temperature at which the reaction takes place and the concentration of oxygen affect the ratio of carbon dioxide to benzoic acid produced in the reaction.

4. The addition of diluents to the reacting gases gave no beneficial results in any of the experiments carried out.

5. Delicate control of air flow and temperature are essential in the type of work herein reported.

6. Anthraquinone and benzaldehyde are by-products of the reaction.

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