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CATALYTIC VAPOUR PHASE OXIDATION OF TOLUENE

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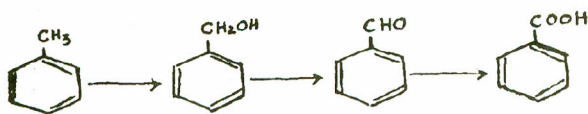
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Toluene, on vapour phase air oxidation in the presence of cobalt naphthenate, as catalyst gives excellent yield of benzoic acid at a temperature of 150° as compared to the oxides, V_2O_5 and mixture of V_2O_5 , MoO_3 , Cr_2O_3 , ThO_3 , CuO and PbO_2 .

Key words: Oxidation, Benzoic acid, Toluene.

Introduction

The oxidation of the methyl group of toluene to produce benzyl alcohol then benzaldehyde and finally benzoic acid is well known [1]. It has also been reported [2] that



oxidation of toluene with air in a air-toluene volume ratio of 80:1 at 260° to 450° over four different catalysts of V_2O_5 at atmospheric pressure gave a mixture of benzene, benzoic acid, maleic anhydride, anthraquinone, cresols and unidentified products. Kumar *et al.* [3] also reported that toluene was oxidized to benzoic acid using V_2O_5 ; $CoMoO_4$, MnO_2 , V_2O_5 and MoO_3 mixture as catalysts duly supported on silica gel, as well as hematite ore and Sn vanadate, converting only 15% toluene at 300°.

Volkkin [4] has reported a systematic study determining various parameters of the oxidation of toluene in vapour phase using metal oxides as catalysts. The optimum toluene air ratio of 1: 2.8 is reported to give good results at a pressure of 0.01 - 0.05 atmosphere at 575°.

The earlier work [5] of liquid phase air oxidation gave very good results and in the light of these results and the findings of Volkkin [4] the present studies have been carried out using five different catalyst supported on sodium silicate and pumice stones to oxidize toluene with air. The results of these studies are reported here and could be used for industrial production of benzoic acid.

Experimental

The experiments were made in standard laboratory glassware and some especially made reaction tubes as described below. The reaction flow diagram for all the experiments carried out is as given in Fig. 1.

Air was passed through a rotameter to measure the flow rate (4 to 6 lit per min). The measured air was passed through pumice stones packed, 0.5 inch dia stainless steel tube of 30 inches length, having controlled electric heating system. The air was heated to the required temperature of 100 to 110° in accordance with the reaction condition selected for the experiment.

Toluene (5 ml per min) was dropped at the bottom of a round bottom one litre flask being heated in an oil bath at the required temperature of 100° or 110°. The oil bath was heated by an isomental so as to control the bath temperature with a variation of $\pm 5^\circ$ only. The measured hot air was led into the oil heated flask to mix the heated air with toluene vapours; air not only works as an oxidant but also as a carrier for the reactants.

The air toluene mixture was then passed through loosely packed catalyst in one inch dia 24 inches long glass tube heated in a tube furnace especially fabricated for these studies.

The resultant vapours were then passed through a copper tubes heat-exchanger, having 15 tubes of one cm dia and 30 inches length duly cooled by water circulation. The vapours from the heat-exchanger were passed into measured quantity of toluene (1000 ml) duly chilled in an ice bath to recover all organic products.

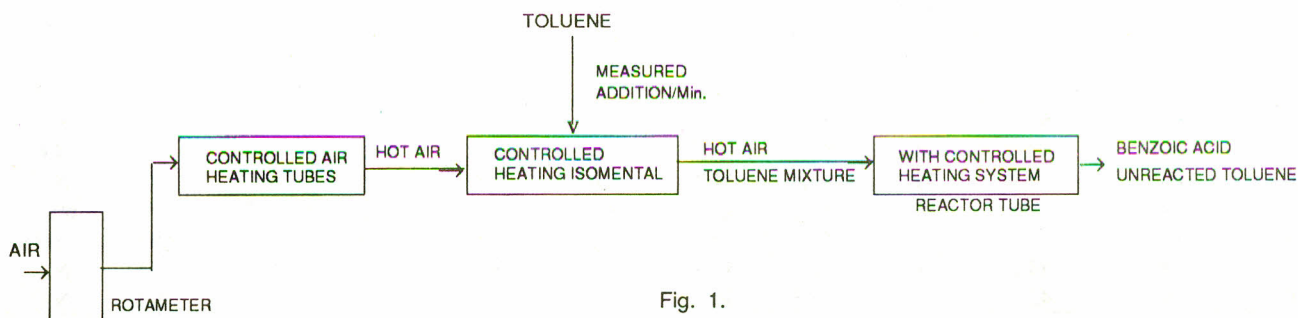


Fig. 1.

In case of low temperature (110 to 170°) cobalt naphthenate reactions, water cooled heat-exchanger was not used and the vapours from the reaction tube were led into measured quantity (1000 ml) of chilled toluene after passing these through an empty flask to air cool the reaction products.

Preparation of Catalysts

Catalyst no.1. Sulphuric acid (550 ml, 17.7%) was added to one mole of vanadium pentoxide and sulphure dioxide gas bubbled through the mixture until a blue colour was formed due to $VOSO_4$.

In a separate beaker sulphuric acid (10%) was added dropwise to four mole solution of sodium silicate (20%) keeping the pH at 5 to 5.5.

The two solutions were mixed and heated slowly with continuous stirring till a thick paste was formed, which was dried in an oven at 150°. The solid obtained was 20% w/w vanadium catalyst which was broken into small irregular pieces.

Catalyst no.2. The oxides of molybdenum, chromium, vanadium and thorium were mixed in a ratio of 90, 3, 2 and 5% by weight (MoO_3 18 gm, Cr_2O_3 0.6 gms, V_2O_5 0.4 gms and $Th O_2$ 1.0 gm). The oxides were mixed with 20% solution of sodium silicate (80 gm). The resultant was heated slowly with continuous stirring till a thick paste was formed. This paste was dried in an oven at 150°. The solid obtained was 20% w/w mixed oxides catalyst which was broken into small irregular pieces.

Catalyst no.3. The oxides of copper, lead, vanadium, manganese and iron were mixed in a ratio of 16, 9, 55,

12.5% and 4.5% by weight respectively (CuO 3.2 gm, PbO_2 1.8 gm, V_2O_5 11.8 gms, MnO_2 2.5 gms and Fe_2O_3 0.9 gm). The mixed oxides were added to a 20% solution of sodium silicate (80 gm) and heated slowly with continuous stirring till a thick paste was formed. The paste was dried at 150° in an oven and the solid mass broken into small irregular pieces. The solid obtained was 20% w/w mixed oxides catalyst.

Catalyst no.4. Vanadium pentoxide 10 gms was mixed with 90 gms of pumice stones by continuous shaking so that powdered oxide was adsorbed on the surface of pumice stones and these stones were heated in an oven for one hour at 150°.

Catalyst No.5. Naphthenic acid ($C_7H_{12}O_2$) (18 gms) was treated with sodium hydroxide (6 gms) dissolved in 250 ml of water to get a clear solution of sodium naphthenate. To the clear solution, concentrated solution of cobalt chloride (9 gms) was added with continuous stirring. The reaction mixture was allowed to stir at room temperature for 2 hr. The precipitate was filtered, thoroughly washed with distilled water and added to 20% solution of sodium silicate (160 gms). The mixture was slowly evaporated with continuous stirring till it formed thick paste which was dried at 150° in an oven. The solid obtained was 10% w/w cobalt naphthenate catalyst which was broke into irregular small pieces.

Results and Discussion

Earlier workers have reported that toluene could be oxidized to benzoic acid in the range of 400° to 600° in the presence of various catalysts. Our work on liquid phase oxidation of toluene in the presence of cobalt naphthenate

TABLE I. VAPOUR PHASE OXIDATION OF TOLUENE TO BENZOIC ACID

Flow rate (ltr/min)	Reactor tube temperature°	Toluene and air mixture temperature 100° at injection					Toluene and air mixture temperature 110° at injection				
		Catalysts used					Catalysts used				
		No.1	No.2	No.3	No.4	No.5	No.1	No.2	No.3	No.4	No.5
4.0	300	32.5	33.5	34.2	34.0	69.5	45.0	46.2	38.4	45.5	70.0
4.0	350	35.2	36.5	38.0	36.5	62.8	47.2	48.2	43.0	48.0	62.0
4.0	400	30.5	31.5	33.0	32.0	59.6	N.C	N.C	37.8	N.C	N.C
4.0	450	29.4	29.9	31.0	30.0	55.0	N.C	N.C	36.0	N.C	N.C
4.5	300	40.1	41.2	42.5	41.0	64.2	55.6	56.9	55.9	57.4	64.8
4.5	350	45.0	46.0	48.0	47.2	60.0	55.4	56.0	56.0	59.0	60.2
4.5	400	42.0	39.0	43.0	40.8	57.0	N.C	N.C	49.0	N.C	N.C
4.5	450	35.0	36.8	41.0	39.5	53.0	N.C	N.C	48.2	N.C	N.C
5.0	300	50.0	51.5	51.9	51.6	63.4	58.2	59.9	61.0	61.9	63.0
5.0	350	53.0	54.0	54.2	54.0	59.0	60.0	61.2	62.5	64.3	59.5
5.0	400	42.0	44.2	46.4	46.0	55.5	N.C	N.C	N.C	N.C	N.C
5.0	450	37.0	39.2	43.0	44.0	52.0	N.C	N.C	N.C	N.C	N.C
6.0	300	52.0	53.2	54.2	54.0	60.5	62.0	63.2	64.2	67.0	60.6
6.0	350	57.0	58.0	59.5	59.0	58.5	64.9	66.2	67.4	68.0	58.2
6.0	400	49.0	51.0	52.0	52.0	54.0	N.C	N.C	N.C	N.C	N.C
6.0	450	42.0	44.0	45.5	48.2	51.2	N.C	N.C	N.C	N.C	N.C

Note:- (1) N. C mean no experime.nt at this temperature carried, (2) % yield is based on benzoic acid obtained only.

as catalyst gave encouraging results that air oxidation to high yields of benzoic acid is possible at low temperature.

The results of our studies are summarised in Tables 1 and 2. Five metal oxide catalysts were selected for comparative study. The reaction temperatures were 300°, 350°, 400° and 450°. At these temperatures the air flow rate was increased from 4 lit/ min to 6 litres per minute thereby increasing the oxygen concentration but reducing the contact time of the reactants with the catalyst. In all the cases the toluene flow rate has been kept constant at 5 ml/ min. The results (Table 1) for the metal oxide catalysts indicate that maximum yield of benzoic acid was obtained at a reaction temperature of 350° and a flow rate of 6 lit/min of air. The benzoic acid yields with the catalyst no.1 to catalyst no.4 have shown identical pattern of increase with increase in temperature from 300° to 350° and a gradual decrease at 400° and 450° when the air flow rate is kept constant. The higher concentration of oxygen (by increase of flow rate of air) improved the % yield at 350°.

Keeping these results in mind four experiments were attempted to increase the oxygen concentration without changing the flow rate of carrier to keep the same contact time and were:

1. Using only O₂ gas as oxidizing agent and carrier of toluene vapours at a flow rate of 4 litres/min.
2. Using a mixture of O₂ gas 3 litres/min. plus air 1 litres/min.
3. Using a mixture of O₂ gas 2 litres/min. plus air 2 litres/min.
4. Using a mixture of O₂ gas 1 litre/min. plus air 3 litres/min.

In all these experiments small explosion occurred due to high oxygen concentration and these experiments were abandoned.

The results of the catalyst no.5 (cobalt naphthenate) indicated that % Yield of benzoic acid dropped with increase of temperature. In the light of these results and that of the liquid phase oxidation we designed a few more experiments (Table no.2) and found that highest % yield of benzoic acid was obtained at 150° with an air flow rate of 4 litres per minute.

TABLE 2. VAPOUR PHASE OXIDATION OF TOLUENE USING COBALT NAPHTHENATE AS CATALYST

Flow rate (lits/min)	Temperature °C	Benzoic acid % yield
3.5	110	75.0
4.0	110	75.9
4.5	110	74.4
3.5	150	85.5
4.0	150	86.2
4.5	150	85.2
3.5	170	83.2
4.0	170	84.3
4.5	170	84.0

This work confirms that benzoic acid of pure quality with a yield of about 86% could be produced from vapour phase toluene air oxidation at a temperature of 150° in continuous manner. The unreacted toluene recovered is not more than 15% as compared to 49% in case of liquid phase oxidation as reported by us earlier. These findings indicate that air oxidation of toluene could easily be utilized for industrial manufacture of benzoic acid from toluene.

References

1. (a) M. Weiler, Ber., **33**, 464, (1900).
(b) D. M. Newitt and J.H. Burgoyne Proc. Roy. Soc. (London) A **153**, 448, 1936, C.A., **30**, 25559.
(c) Torromura Bull Instt. Phys. Chem. Research (Tokyo) **21**, 774; C.A. **41**, 5465g.
(d) R.D. Abell, J. Chem. Soc., 1379 (1951).
2. H. Pichler and F. Obenaus, Tech Hochschule Karlsruhe Gen. Brennstoff Chem., **54** (4), 97-013, 1964; C.A. **61**, 4239b.
3. R.N. Kumar, G.N. Bhat and N. R. Kuloor, Indian Chem. Eng., **7** (4). Trans., 78-82, 1965; C.A. **64**, 10448a.
4. N. I. Volknkin Zh. Prikl Khim. **39** (12), 2783-7 (1966), C.A. **67**, 2850i.
5. (a) J. K. Sluis, Van, Chem. Prods., **20**, 191 (1957).
(b) N. Uri. Nature **187**, 746 (1969).
(c) T. A. Chaudri, M. Ahmed and M.A. Akhtar Pak. j. sci. ind. res. S. No.4423 (submitted 25th May 1989) and references cited therein.