SYNTHESIS OF BENZOIC ACID
FROM CHLOROBENZENE UNDER PRESSURE

By S. K. PALIT and N. TRIPATHY*

Conversions as high as 76.26% and 80-85% of chlorobenzene to benzoic acid were obtained when chlorobenzene was carboxylated with carbon monoxide and water at high pressure with nickel iodide-silica gel catalyst (Ni:SiO₂ = 50:50) and without any catalyst (thermal) respectively, at the optimum temperature and pressure; these optima were much higher for the latter than for the former process. The lower yield in the catalytic process could be improved to some extent if the catalytic reaction was carried out at a pressure, reached by introducing nitrogen in addition to the usual input of carbon monoxide, almost equal to the optimum pressure of the thermal process.

Introduction

The possibility of synthesising various aromatic carboxylic acids, esters etc. of industrial importance by the carboxylation (or carboxylation) of aryl halides under pressure with mainly nickel carbonyl as catalyst, has been disclosed in various patents. In one such patent, Kröper et al. have claimed that benzoic acid and its esters can be synthesised from bromo- and chloro-benzenes in a similar way. Romanovskii & Artemev in a paper on carboxylation of dichlorobenzene, have also claimed to have obtained benzoic acid by the same procedure. However, as both these papers are lacking in detail and because of the industrial importance of benzoic acid and the superior catalytic activity of nickel iodide-silica gel catalyst (Ni : SiO₂ = 50 : 50) to the carbonyls, a detailed study of the synthesis of benzoic acid from chlorobenzene, carbon monoxide and water with and without this catalyst has been carried out.

Thermodynamics of the reaction

C₆H₅Cl(g) + CO(g) + H₂O(g) = C₆H₅COOH(g) + HCl(g)

The effects of temperature and pressure on the equilibrium constant of this reaction are given in Table I.

**Table 1**

<table>
<thead>
<tr>
<th>Pressure, atm.</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>0.7789</td>
<td>0.716</td>
<td>0.657</td>
<td>0.589</td>
<td>0.521</td>
<td>0.454</td>
<td>0.390</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.16</td>
<td>4.78</td>
<td>4.41</td>
<td>4.05</td>
<td>3.71</td>
<td>3.38</td>
<td>3.06</td>
</tr>
<tr>
<td>K⁺, × 10⁻²</td>
<td>2.34</td>
<td>1.71</td>
<td>1.17</td>
<td>0.84</td>
<td>0.59</td>
<td>0.40</td>
<td>0.28</td>
</tr>
<tr>
<td>K⁺, × 10⁻²</td>
<td>0.9789</td>
<td>0.8236</td>
<td>0.6789</td>
<td>0.554</td>
<td>0.440</td>
<td>0.336</td>
<td>0.232</td>
</tr>
</tbody>
</table>

*K⁺ = K⁺, where K⁺ is the equilibrium constant at 1 atm; K⁺ is the equilibrium constant for different pressures at constant temperature and K⁺ = γ TimeKC₆H₅Cl × γ TimeHC₆H₅COOH/γ TimeHCl × γ TimeH₂O and γ = f, where f is the fugacity of the gas and γ is the fugacity of the liquid.

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As values of the free energy and heat of formation of benzoic acid in the gaseous state and the heat capacities of benzoic acid and chlorobenzene were not available, these were calculated by the group contribution method.\(^5\)

For the calculation of the effect of pressure on the equilibrium constant at 200\(^\circ\), the fugacity co-efficients of the various compounds were evaluated from the chart proposed by Lydersen et al.\(^6\) and corrected for the different critical compressibilities.\(^7\) The temperature of 200\(^\circ\) was selected so as to avoid the unreliable reduced temperature range of 0-8-1/2 at reduced pressures above 1.2.\(^7\) From Table I(b), it is seen that the equilibrium constant contrary to expectation, fluctuated in value. This could be due to the influence of pressure on the fugacity co-efficients of the various compounds, but as the reaction proceeds with volume decrease it is obvious that the equilibrium conversion would increase with pressure.

**Experimental**

A high-pressure rocking autoclave of 270 ml capacity at 25\(^\circ\)C and 1 atm pressure having an angular play of 15\(^\circ\) with 45 oscillations per min was used. The product release assembly and other experimental set-up were similar to those described by Bhattacharyya and co-workers.\(^8,9\)

Very pure carbon monoxide was prepared in the laboratory by the same method and the same precautions were taken as in the earlier work.\(^5,6\) All other chemicals used were of analytical grade.

The catalyst, nickel iodide supported on silica gel containing 84-16\% of nickel iodide (Ni : SiO\(_2\) = 50 : 50), used in this work, was prepared according to the method of Bhattacharyya & Sourirajan.\(^9\)

**Liquid products**

The liquid products of the reaction consisted of benzoic acid, formic acid and benzaldehyde (in a few cases under non-catalytic conditions only), together with the unconverted chlorobenzene and water. Occasionally minute traces of hydrochloric acid, nickel and iron salts were also present. Individual components were identified by their melting points and mixed melting points wherever possible, by forming suitable derivatives and by paper and gas chromatography.

The liquid product mixture was cooled to about 0\(^\circ\) and filtered. The residue, containing benzoic acid and other solid impurities, was treated with alcohol and subsequently titrated with standard alkali to estimate benzoic acid. A quantity of the filtrate was steam-distilled to eliminate the impurities. In the distillate, benzaldehyde was estimated by the 2:4 dinitrophenyl hydrazine method; formic acid by titration with alkaline potassium permanganate and then subtracting the amount consumed by benzaldehyde (if present) from the above titration value; and finally benzoic acid was determined by subtracting the acidity due to formic acid from the total free acidity of the distillate. As the amount of hydrochloric acid or the chlorides, determined by Volhard's method after acidifying a part of the filtrate with nitric acid, was almost negligible, it did not interfere with the analyses of the other products.

**Gaseous products**

The gaseous product was found to contain carbon dioxide, hydrogen and saturated hydrocarbons (methylene was the chief constituent) together with carbon monoxide. Analysis was carried out with a standard Orsat gas analyser and the results were confirmed when necessary by gas chromatography.

**Results and discussion**

As some preliminary investigations revealed that benzoic acid was produced even when the experiments were conducted in the absence of any catalyst (thermal), the determination of the optimum reaction conditions at which the yield of benzoic acid would be a maximum was carried out for both the catalytic and non-catalytic conditions. The results are recorded in Figs 1-4 and Tables II-IV. Since the particular reactions by which carbon dioxide and saturated hydrocarbons were formed during the synthesis reactions could not be represented by balanced equations, the yields of these gases were calculated on the basis of the percentage of total input carbon (from chlorobenzene and carbon monoxide) that could be accounted for by the carbon of the respective gas and have been given as 'percentage carbon conversion'. Similarly the yield of gaseous hydrogen has been expressed as 'percentage hydrogen conversion'.

**Effect of pressure**

The influence of pressure at different temperatures was studied under both catalytic and non-catalytic conditions by varying the input of all the reactants by the same proportion so that their mole ratio remained constant in all the experiments (Fig. 1). When the temperature was changed by 90\(^\circ\) (220-310\(^\circ\)) in experiments with catalyst, the optimum pressure did not increase to the extent that was noted by only a 50\(^\circ\) rise (310-360\(^\circ\)) under non-catalytic conditions. This was probably because the temperature (360\(^\circ\)) was very close to the critical temperatures of water and chlorobenzene. With increasing pressures the yields of benzaldehyde, formic acid and the gaseous decomposition products increased steadily in all cases. However under catalytic conditions the yields of formic acid and gaseous decomposition products were higher than those under non-catalytic conditions (Fig. 2).

**Effect of temperature**

The optimum temperature of 295\(^\circ\) under catalytic conditions was much lower than 360\(^\circ\) for non-catalytic conditions (Fig. 3). In both cases, the yields of benzoic acid and gaseous decomposition products increased with rise of temperature whereas the yield of formic acid decreased. Of the decomposition products the yields of carbon dioxide, saturated hydrocarbon and hydrogen, increased steadily from 12.9-42.8\% \(^6\) 4.7-6.7\% \(^6\) and 0.5-30.3\% respectively for catalytic conditions, whereas for the non-catalytic conditions, the corresponding values were respectively 19.2-31.2\%, 0.11-6.6\% and 0.11-6.6\% over the temperature ranges investigated.

**Effect of residence time**

With increase in residence time the yield of benzoic acid passed through an optimum at three hours in both cases. However in the catalytic synthesis the yield of benzoic acid was less affected by residence time than when under non-catalytic conditions. The yield of formic acid increased as residence time was increased for catalytic synthesis, while the reverse was true for non-catalytic synthesis. The yields of gaseous decomposition products increased steadily with residence time and their yields increased almost by the same amounts in the two different synthetic conditions for the same variation in residence time.
Fig. 1. Effect of pressure on yields of benzoic acid in both catalytic and thermal processes

With catalyst: ○○○ 5 ml at 310°C; ●●● 10 ml at 220°C
Non-catalytic: ■■■ at 360°C; △△△ at 310°C
Mole ratio of reactants: CO : H₂O : C₆H₅Cl = 1 : 1 : 29 : 0.0114
Residence time = 3 h

Fig. 2. Effect of pressure on yields of gaseous decomposition products at 310°C in both catalytic and thermal processes

With catalyst: ○○○ CO₂; ■■■ H₂; ●●● saturated hydrocarbon
Non-catalytic: ○○○ CO₂; ■■■ H₂; △△△ saturated hydrocarbon
Reaction conditions are the same as in Fig. 1

Fig. 3. Effect of temperature on yields of benzoic acid in both catalytic and thermal processes

Mole ratio of reactants CO : H₂O : C₆H₅Cl = 2 : 15 : 2 : 77 : 0.0246
With catalyst: ○○○ 5 ml at 5700–9400 lb/in.²
Non-catalytic: ■■■ at 4000–9600 lb/in.²

Fig. 4. Effect of residence time on yields of benzoic acid in both catalytic and thermal processes

With catalyst: ○○○ 10 ml at 295°C and 6700 lb/in.²
Non-catalytic: ■■■ at 360°C and 9100 lb/in.²

Table II

<table>
<thead>
<tr>
<th>Input of reactant, moles</th>
<th>Pressure, lb/in²</th>
<th>Yield of benzoic acid, %</th>
<th>Percentage of carbon converted to CO₂</th>
<th>Percentage of input hydrogen converted to gaseous hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>H₂O</td>
<td>C₆H₅Cl</td>
<td>Catalytic</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-----</td>
<td>------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>2-33</td>
<td>1-66</td>
<td>0-0246</td>
<td>6500</td>
<td>8200</td>
</tr>
<tr>
<td>2-15</td>
<td>2-77</td>
<td>0-0246</td>
<td>6750</td>
<td>9100</td>
</tr>
<tr>
<td>1-97</td>
<td>3-89</td>
<td>0-0246</td>
<td>6900</td>
<td>9150</td>
</tr>
<tr>
<td>2-15</td>
<td>2-77</td>
<td>0-0492</td>
<td>8800</td>
<td>67-11</td>
</tr>
<tr>
<td>2-04</td>
<td>3-33</td>
<td>0-0492</td>
<td>6700</td>
<td>31-17</td>
</tr>
</tbody>
</table>

Reaction conditions: catalytic—with 10 ml nickel iodide:silica gel catalyst at 295°C for 3 h; thermal (non-catalytic)—at 360°C for 3 h.
Effect of change in reactant ratio

As is evident from Table II, the optimum yield for both catalytic and non-catalytic syntheses was obtained when the input of carbon monoxide, water and chlorobenzene were 2:15, 2:7 and 0:0246 moles respectively. With increase in the input and mole ratio of water and carbon monoxide, the yields of carbon dioxide and methane increased steadily for both conditions whereas hydrogen did not follow any particular trend. With increasing amounts of water the yield of formic acid increased for catalytic reactions whereas for non-catalytic reaction there was little change.

Effect of the quantity of catalyst

It is evident from Table III that an increase in the amount of catalyst beyond 10 ml (13 g) did not have any appreciable effect on the yield of benzoic acid or gaseous decomposition products. The yield of formic acid (not presented in Table III) was highest with 15 ml of the catalyst, which incidentally also gave the optimum yields of benzoic acid.

**TABLE III**

<table>
<thead>
<tr>
<th>Catalyst volume, ml</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of benzoic acid, %</td>
<td>72-26</td>
<td>74-94</td>
<td>76-26</td>
<td>75-89</td>
</tr>
<tr>
<td>Amount of carbon converted, %</td>
<td>23-7</td>
<td>23-8</td>
<td>24-4</td>
<td>25-8</td>
</tr>
<tr>
<td>(i) to CO₂</td>
<td>4-8</td>
<td>9-3</td>
<td>9-4</td>
<td>9-5</td>
</tr>
</tbody>
</table>

Reaction conditions: Pressure 6750 lb/in² at 295°C for residence period of 3 h; mole ratio of reactants CO₂ : H₂O : C₆H₅Cl = 2-15 : 2-77 : 0:0246; 10 ml of catalyst weighs 13 g.

**TABLE IV**

<table>
<thead>
<tr>
<th></th>
<th>Thermal</th>
<th>Catalytic</th>
<th>Catalytic (reaction pressure raised by nitrogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature, °C</td>
<td>360</td>
<td>295</td>
<td>295</td>
</tr>
<tr>
<td>Input pressure, lb/in²</td>
<td>2500</td>
<td>2500</td>
<td>3300*</td>
</tr>
<tr>
<td>Reaction pressure, lb/in²</td>
<td>9100</td>
<td>6750</td>
<td>9700</td>
</tr>
<tr>
<td>Yield of benzoic acid, %</td>
<td>80-85</td>
<td>76-26</td>
<td>79-14</td>
</tr>
<tr>
<td>Amount of carbon converted to:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) CO₂, %</td>
<td>26-1</td>
<td>24-4</td>
<td>17-8</td>
</tr>
<tr>
<td>(ii) saturated hydrocarbon, %</td>
<td>10-3</td>
<td>9-4</td>
<td>0-7</td>
</tr>
<tr>
<td>Amount of hydrogen converted to gaseous hydrogen, %</td>
<td>10-2</td>
<td>9-2</td>
<td>0-2</td>
</tr>
</tbody>
</table>

*3500 lb/in² initial pressure was built up by an input of 2500 lb/in² carbon monoxide and 1000 lb/in² nitrogen.

Reaction conditions: mole ratio of reactants and residence time as in Table III; volume of catalyst 15 ml.

Conclusions

In the systems studied it was found that nickel iodide on silica gel (Ni : SiO₂ = 50 : 50) is an efficient catalyst, giving a much lower optimum reaction pressure and temperature, 6750 lb/in² and 295°C respectively, compared with the values 9100 lb/in² and 360°C respectively, under non-catalytic conditions (Table IV) with only about 4% loss in the benzoic acid yield.

When the optimum input pressure of 2500 lb/in² at 25°C in the catalytic study was boosted with nitrogen to an input pressure of 3500 lb/in² at 25°C so that the final reaction pressure of 9700 lb/in² was almost identical with the optimum pressure under non-catalytic conditions, the percentage conversion of chlorobenzene to benzoic acid increased to nearly the same value as that under non-catalytic conditions (Table IV), indicating the pressure dependence of the reaction.

Production of formic acid, probably by the interaction of carbon monoxide with water, was favoured to a greater extent in the presence of the catalyst. Similarly decomposition or other side reactions leading to the formation of various gaseous products, were more favoured in presence of the catalyst.

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