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Selective Bromination of p-Xylene via Homogeneous Catalysis: Influence of Reaction Parameters on 2,5-Dibromo- p-Xylene Formation

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Abstract. In general, homogeneous catalysis signifies reactions with soluble catalysts that are of the same phase as of the reactants in order to decrease the activation energy and increase the reaction rate. The aromatic halogenation substitution reaction of p-xylene to the multi-halogenated derivatives is a well-known reaction that has been studied over years. However, the recent advances in porous materials (e.g., MOFs) have re-focused the spot again on such a reaction so as to functionalize those materials. This study is concerned with the homogeneous catalytic bromination of p-xylene to 2,5-dibromo-p-xylene along with its separation and purification. Using Ferric chloride hexahydrate as catalyst, the effect of variating the bromine amount, the reaction temperature, and the reaction time have been selectively studied. The products were characterized using XRD, FTIR, and H^1 NMR Spectrometer. The best yield of 2,5-dibromo-p-xylene is at bromine/p-xylene ratio of 2:1.

Keywords: Catalysis; Bromination; Halogenation; p-xylene; 2,5-dibromo-p-xylene.

1. Introduction

2,5-dibromo-p-xylene is of great industrial importance as an agrochemical and in pharmaceuticals [1]. In material science, it has regained its importance for its role in the development of functionalized linkers (e.g., 2,5-dibromo-terephthalic acid) in metal-organic frameworks (MOFs) production [2]. Direct halogenation reaction of terephthalic acid to 2,5-dihalo-terephthalic acid is not the most conventional path offered due to the presence of the two carboxylic groups at the para- position with respect to each other. Despite being a meta-directing group, the carboxylic group is a deactivating group that slow down the halogenation reaction. With the two carboxylic groups found in terephthalic acid, the achievement of the halogenated product is relatively low [3]. On the contrary, an alkyl group is an activating group while being an ortho- and para- directing group [3]. Hence, researchers targeting halogenated terephthalic acid start with p-xylene. The halogenation of p-xylene, followed by the oxidation of alkyl groups, ultimately leads to the desired product, achieving greater selectivity and yield [4].

The bromination of p-xylene occurs via a typical mechanism of electrophilic aromatic substitution, characterized by a series of sequential bromination reactions, according to the mechanism shown in Fig. 1. Bromine's poor electrophilicity makes it difficult to react with benzene. A strong Lewis acid, such as $FeCl_3$, catalyzes the process by forming an intermediate complex that responds similarly to Br^+ (eqn. 1). Through coordination with the catalyst, the intermediate complex becomes a stronger electrophile with a weaker Br-Br bond and a partial positive charge on one of the bromine atoms. When it attacks the benzene ring as an electrophile, it forms a sigma complex with a delocalized positive charge on the ring as a result of the bromine addition (eqn. 2). The bromide ion from $[FeCl_3Br]^-$ serves as a weak base, removing a proton out of the sigma complex, producing 2-bromo-p- xylene, and regenerating the catalyst (eqn. 3). Further bromination reaction results in the dibromo-, tribromo-, and tetrabromo-p-xylene, respectively [3].

In the first step of the bromination reaction, 2-bromo-p-xylene is produced as a result of the methyl group being an ortho- and para- directing group. So, in case of p-xylene, the first bromine atom will

substitute one of the four hydrogen atoms of the benzene ring at an equal probability resulting in the exact same product, namely 2-bromo-p-xylene.

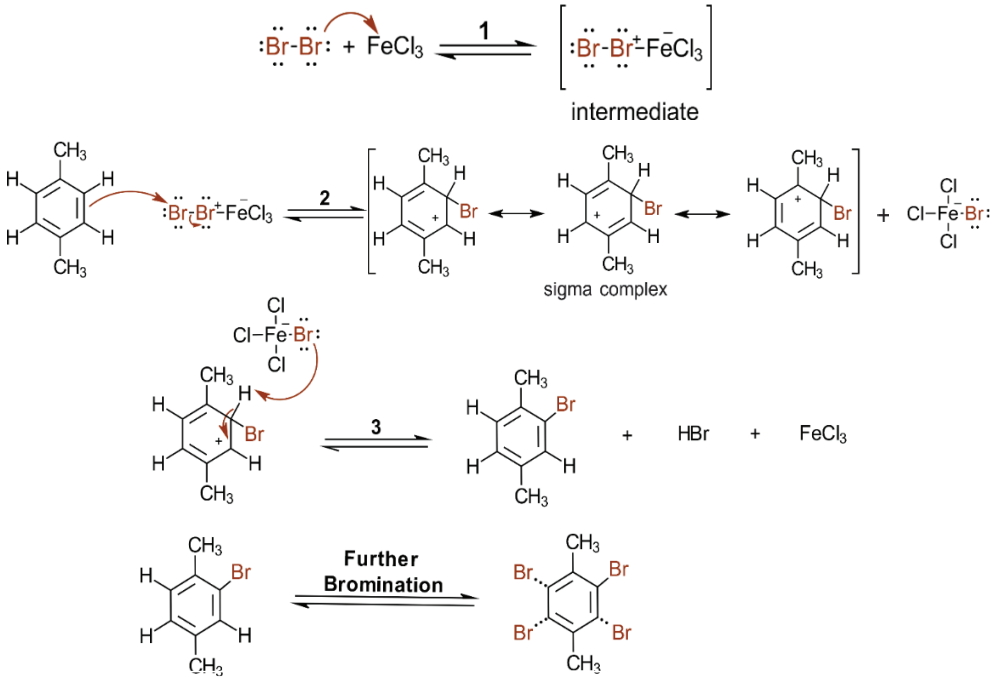

Figure 1. The stepwise substitution mechanism adopted during bromination of p-xylene.

The second bromination step may produce one of three isomers (i.e., 2,5-dibromo-p-xylene, 2,3-dibromo-p-xylene, and 2,6-dibromo-p-xylene; Fig. 2) [5, 6]. However, the predominant product of these isomers is 2,5-dibromo-p-xylene since the bromine atoms are symmetrically positioned which makes the structure less sterically hindered, less electronically strained, and hence, more stable [3].

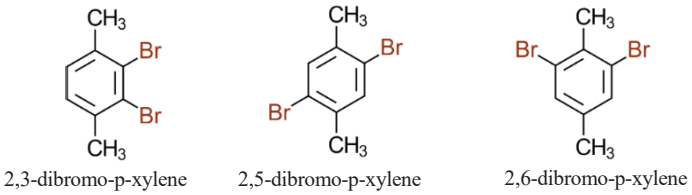

Figure 2. Different structural isomers taking place during second bromination step.

This study does not concentrate on the bromination reaction of p-xylene; rather, the primary objective is to investigate the formation of 2,5-dibromo-p-xylene as the principal product and its relationship with various reaction parameters.

2. Experimental Work

2.1. Materials

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$, ≥ 99%) obtained from Sisco Research Laboratories Pvt. Ltd. (SRL, India) was employed as catalyst, representing the Lewis acid. Bromine (Br_2, 99%) was purchased from SD Fine-Chem Ltd. (India) and p-xylene (C_8H_{10}, ≥ 99%) was purchased from VWR Chemicals BDH®, UK. All chemicals were used as received with no further processing or purification, and all experiments were conducted under ambient atmosphere unless otherwise stated.

2.2. Experimental Setup

The reaction was conducted in a glassware setup assembled as shown in Fig. 3 inside a fume hood. A round-bottom flask, where the reaction is taking place, was clamped into a water bath over a hot plate. A graduated dropping funnel was also clamped over the reaction flask. The water bath was stirred via a magnetic stirrer to ensure homogenous heat transfer to the walls of the reaction flask.

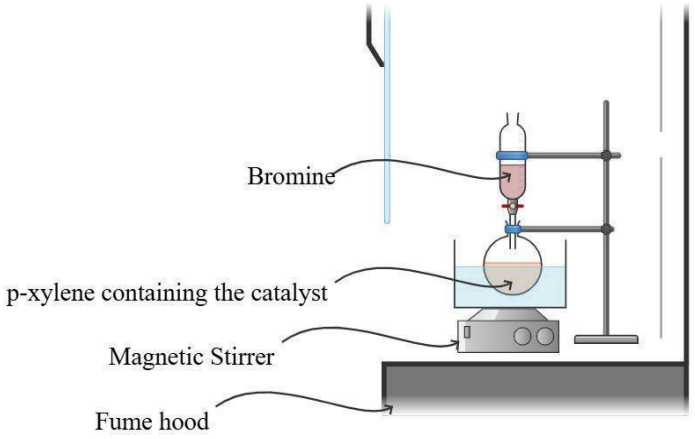

Figure 3. The assembled glassware setup for the catalyzed bromination reaction.

2.3. Method

First, 2.7 g (10 mmol) of ferric chloride hexahydrate was directly weighed into the reaction flask. Then, 62 ml (500 mmol) of p-xylene was added to the flask and the flask was stirred for 15 min. The flask was then clamped into the water bath so that the water level exceeds that of p-xylene. Bromine was added to the reaction medium drop-by-drop while stirring. The reaction was maintained at a specific temperature with the help of the water bath while the reaction temperature was monitored using a thermocouple. The reaction time represents the time measured right after the bromine is fully added to the reaction flask till the specified duration. The reaction was conducted in safety cabinet fume hood to decrease the exposure to bromine vapors.

2.3.1. Variation of precursors' molar ratio (Bromine amount). for these series of experiments, the amount and type of catalyst (10 mmol $FeCl_3 \cdot 6H_2O$), the amount of p-xylene (62 ml, 0.5 mol), the reaction temp. (20°C) and time (3 h) were maintained constant. While the amount of the added bromine with respect to p-xylene is the only variable to track. The added bromine amount ranged from 26 ml – 64 ml yielding a stoichiometric ratio, with respect to p-xylene, ranging from 1:1 to 1:2.5, according to Table 1).

Table 1. *The used precursors' amounts with respect to the stoichiometric ratios.*

Exp. No.	(P-xylene: Bromine) Molar ratio	P-xylene [ml] (mol)	Bromine [ml] (mol)
1	1: 1	62 (0.5)	26 (0.5)
2	1: 1.5	62 (0.5)	39 (0.75)
3	1: 2	62 (0.5)	52 (1)
4	1: 2.5	62 (0.5)	65 (1.25)

2.3.2. Variation of the reaction time. After assigning the convenient precursors' ratio, the effect of the reaction time was studied. The reaction duration varied from 1 h - 5 h, with a step of 1 h. As mentioned above, the reaction time refers to the time measured right after the bromine was fully added to the reaction flask until the specified duration.

2.3.3. Variation of the reaction temperature. The effect of the reaction temperature on the obtained products was also studied, whereby the applied reaction temperature ranged from 10°C - 50°C, while keeping all other reaction variables fixed at the optimum values determined from the previous experiments.

2.4. Characterization

Powder x-ray diffraction (PXRD) data was obtained using Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λKα = 1.5406 Å). The source was operated at a tube current of 30 mA, and a voltage of 40 kW. Samples were scanned over a 2θ range from 5º to 90º at a rate of 0.02º/s. Fourier-transform infrared (FTIR) spectra were collected over an ATR crystal using a Perkin Elmer spectrometer. The spectrum was recorded over the range of 4000 cm^{-1} - 400 cm^{-1} with a resolution of 4 cm^{-1}. The obtained spectrum is the average of 32 scans. The H^1 NMR spectra was obtained using 400 MHz NMR Spectrometer with pulse width of 10 μs (90ºC pulse), relaxation delay of 2 s -3 s, spectral width from 0 ppm to 14 ppm, number of scans 32 scans and acquisition time of 2 s - 4 s. The sample was dissolved in 5 mg - 10 mg deuterated dimethyl sulfoxide (DMSO-d_6).

3. Results and Discussion

P-xylene is a colorless liquid at ambient temperature, exhibiting immiscibility with water and possessing a boiling point of approximately 140°C [6]. Monobromo-p-xylene is also a liquid which is usually colorless, or of a faint yellow color, with a boiling point around 200°C [7]. Higher brominated compounds along with their isomers are usually solids [8]. Based on the clear differences in the products' properties, separation and purification steps are usually taking place through distillation.

Usually, the reaction ends up with a liquid-solid suspension. By the end of the reaction, solid components were found settling at the base of the reaction flask, which may contain undissolved ferric chloride catalyst, some higher brominated products, and other reaction residuals. The reaction products were first filtered, and the filtrate was transferred to a distillation flask of a simple distillation setup. The cake was washed multiple times with deionized water to exclude the excess dissolvable catalyst. The remaining solids were transferred also to the distillation flask.

Throughout the distillation process, the temperature was initially set at 110°C to remove any contained water and low-boiling point residuals and the collected products (if any) should be discarded. Then, continuous heating takes place, and the products were collected at the point where the temperature settles for a while. Since the targeted 2,5-dibromo-p-xylene product is solid of a relatively low melting point ranging from 72°C - 75°C [9], warm water of 80°C was used as a cooling liquid within the condenser to prevent the product's crystallization and the clogging of the condenser during the distillation process.

3.1. Variation of precursors' molar ratio (Bromine amount)

In the first experiment that contained a stoichiometric amount of the reaction precursors (equivalent molar ratio, 1:1), a very few distillate-liquid droplets were collected at around 145°C (product 1) representing the unreacted p-xylene. Then, the second distillate liquid was collected at around 205°C, comparable to the boiling point of 2-bromo-p-xylene (product 2). In this experiment the second distillate was the major product. Finally, the third distillate was collected as a liquid around 270°C, which quickly crystalize in the collected flask giving off-white crystals, representing the dibromo-p- xylene products (isomers, product 3). The distillation ends up with very fine traces of dark solids in the main distillation accounting for multi-brominated products (product 4).

Increasing the added amount of bromine to 1.5 molar ratio with respect to p-xylene and following the previous regime, a closely equal amount of the collected second distillate (product 2) was obtained and a recognizable increase of the collected third distillate (product 3). Further increase in the bromine amount to 2 and 2.5 molar ratios led to a noticeable decrease in the collection of the second distillate liquid (product 2) along with a significant increase in the collection of the third distillate as the major product (product 3). However, in both experiments, the amount of the remaining residuals (product 4) obtaining the third distillate also increased, giving rise to lightly grey solids that melt and evaporate above 300°C, suggesting higher brominated products.

The FTIR spectrum of product 1 (Fig. 4.i-a) is in a good agreement with that of pure p-xylene, whereby the aromatic C-H stretching vibrations appeared in the region of 3100 cm^{-1} – 3000 cm^{-1}, the aliphatic C-H stretching of the methyl (-CH_3) groups is observed between 2960 cm^{-1} – 2850 cm^{-1}. The aromatic C=C stretching vibrations of the benzene ring produce strong absorption bands at approximately 1600 cm^{-1} and 1500 cm^{-1}. Methyl group bending vibrations are evident at 1460 cm^{-1} (asymmetric) and 1375 cm^{-1} (symmetric). Additionally, a distinct band near 820 cm^{-1} corresponds to the out-of-plane C-H bending mode, characteristic of para-substituted benzene rings. The region between 1150 cm^{-1} – 1050 cm^{-1} exhibits medium-intensity peaks attributed to the C-H rocking vibrations of the alkyl substituents. Collectively, these spectral features align with the molecular structure of p-xylene, supporting its identification and confirming the expected functional groups.

For products 2 and 3 (Fig.4.i-b, i-c), the FTIR spectra exhibited similar characteristic absorption bands to that of p-xylene with slight differences. For product 2 (Fig. 4.i-b), a slight shift along with an intensity variation in the C-H bending and C-H rocking regions (900 cm^{-1} – 700 cm^{-1} and 1150 cm^{-1} – 1050 cm^{-1}, respectively) took place as a result of the presence of a single bromine atom, suggesting the formation of 2-bromo-p-xylene. For product 3, on the other hand, (Fig. 4.i-c) the further modification of the out-of-plane C-H bending vibrations, with a strong absorption near 810 cm^{-1}, indicative of two bromine substituents in the para orientation, referring to the formation of 2,5-dibromo-p-xylene. The progressive bromination also leads to subtle shifts in the methyl bending vibrations (1460 cm^{-1} and 1375 cm^{-1}) due to electronic effects. These spectral variations confirm the stepwise bromination of p- xylene and the influence of bromine substitution on vibrational modes.

The H^1-NMR spectra of the obtained products confirmed the results of the FTIR spectra (Fig. 4. ii), whereby for product 1, a singlet around 2.25 ppm took place referring to chemical equivalence of the two methyl groups, confirming the structure of p-xylene (Fig. 4.ii-a). The four aromatic protons, symmetrically positioned, appear as a singlet near 7.00 ppm due to the high symmetry of the molecule. Product 2 agreed well to the simulated pattern of 2-bromo-p-xylene, in which the introduction of a bromine atom disrupts the symmetry of p-xylene, resulting in an AA'BB' splitting for the aromatic protons, typically appearing as three triplets in the 7.1–7.5 ppm region (Fig. 4.ii-b). The methyl protons remain a singlet but experienced a downfield shift due to the bromine's electron-withdrawing effect. For product 3, further reduction in symmetry leads to more pronounced deshielding of the aromatic protons, with their signals shifting further downfield, typically appearing as two distinct doublets in the 7.2 – 7.7 ppm region (Fig. 4. ii-c). The methyl singlet also shifts slightly further downfield compared to the mono-brominated compound. Hence, confirming the achievement of the targeted product 2,5-di-bromo-p-xylene as the main product (product 3). Also, these changes highlight the electronic effects of bromine substitution and confirm the stepwise bromination of p-xylene.

The X-ray diffraction (XRD) pattern of product 3 came also in great agreement to that of 2,5-dibromo-p-xylene (Crystallography open database, CIF#:264182), revealing distinct crystalline features influenced by the presence of two bromine atoms on the benzene ring. The diffraction pattern exhibits sharp, well-defined peaks, indicative of a highly ordered crystalline structure. Compared to p-xylene, the introduction of bromine atoms increases molecular packing efficiency due to enhanced intermolecular interactions, such as halogen bonding and van der Waals forces. The most intense diffraction peaks appear at characteristic 2θ values, typically in the 10°–30° range, corresponding to

the specific crystal lattice parameters of the brominated compound (Fig. 5). The peak shifts and increased intensities relative to p-xylene suggest a modification in unit cell dimensions, reflecting the impact of bromine substitution on molecular packing. The absence of broad peaks confirms the absence of significant amorphous content, further supporting the crystalline nature of 2,5-dibromo-p- xylene. These structural insights from XRD provide valuable confirmation of the compound's purity and crystallographic integrity.

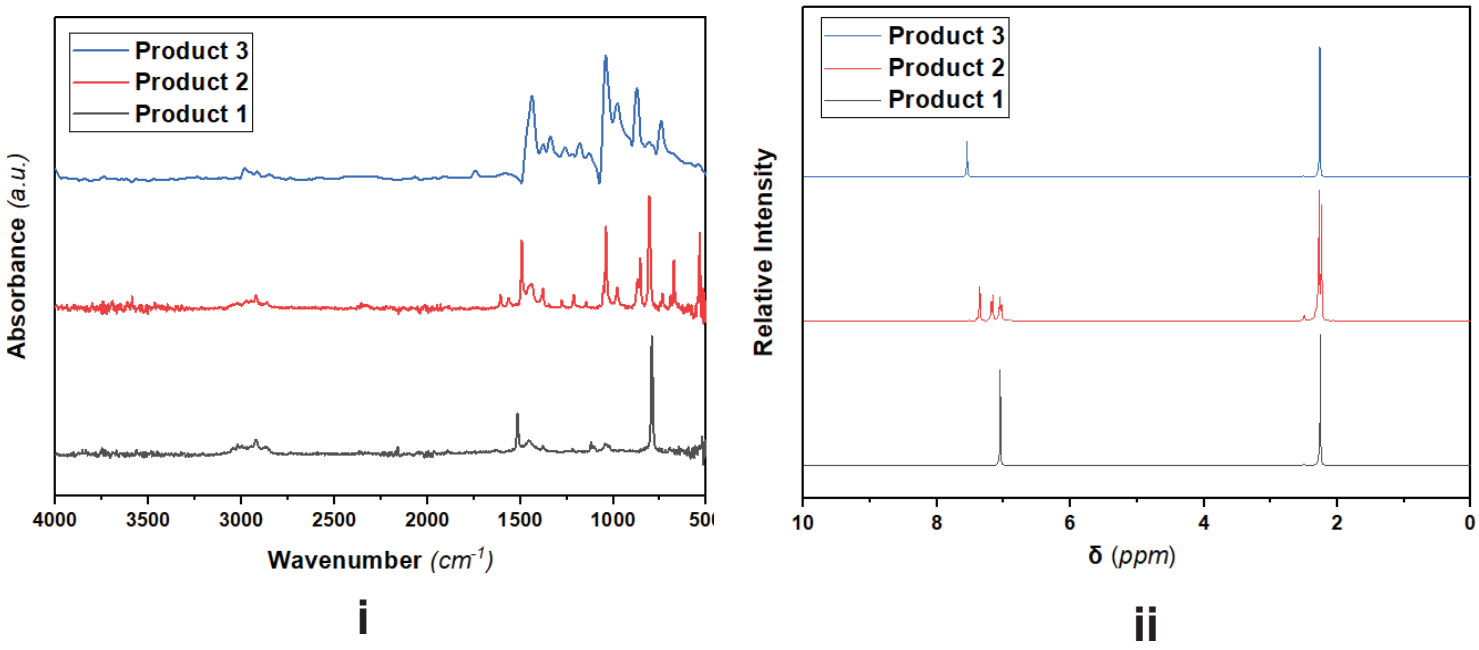

Figure 4. FTIR Spectra (i) and H^1 NMR Spectra (ii) for (a) product 1, (b) product 2, and (c) product 3.

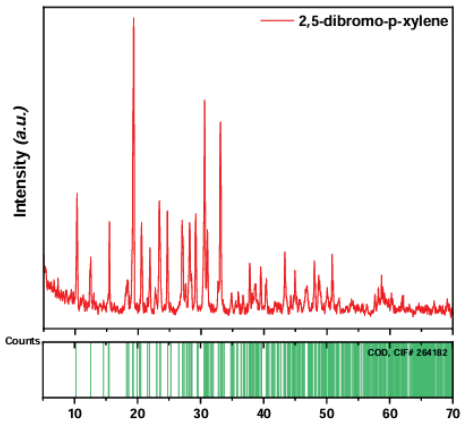

Figure 5. XRD pattern of product 3 compared to 2,5-dibromo-p-xylene (CIF# 264182).

As a summary, characterizing the reaction products confirmed the presence of unreacted p-xylene as product 1, the achievement of 2-bromo-p-xylene as product 2, and 2,5-dibromo-p-xylene as product 3. Higher brominated products were excluded as they were beyond the scope of this study. Experimental results revealed that, the yield of 2,5-dibromo-p-xylene increased with increasing bromine/p-xylene molar ratio (Table 2). The maximum yield of 2,5-dibromo-p-xylene was achieved at a bromine molar ratio double to that of p-xylene (Fig. 6). Higher molar ratio decreases the yield of the 2,5-dibromo-p-xylene to the detriment of higher brominated products (such as 2,3,5-tribromo-p-xylene).

Table 2. Effect of the added bromine amount on the yield of the reaction products

Exp. No.	p-xylene: Br molar ratio	Yield (%)		
		Unreacted p-xylene	2-bromo-p-xylene	2,5-dibromo-p-xylene
1	1: 1	6.5	61.2	3.8
2	1: 1.5	4.9	46.6	28.0
3	1: 2	3.3	5.7	60.6
4	1: 2.5	2.5	2.5	40.3

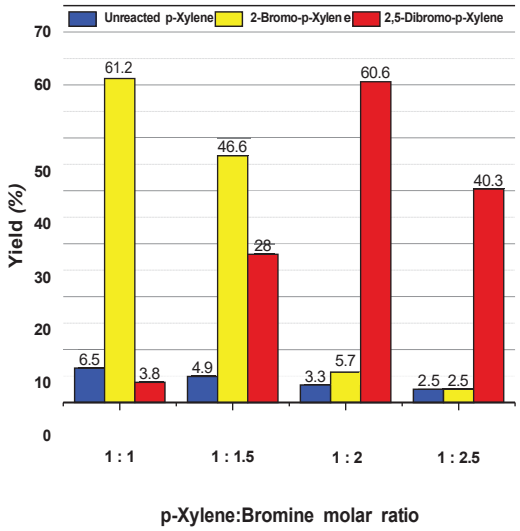

Figure 6. Effect of the added bromine amount on the yield of different products.

3.2. Variation of the reaction time

In the previous set of experiments, the reaction time was maintained at 3 h. Reconducting the reaction while adjusting the p-xylene to bromine molar ratio at 1:2 (max. yield of 2,5-dibromo-p-xylene) and studying the effect of changing the reaction time on that yield was also performed. Decreasing the reaction time to 2 h resulted in a lower product yield of 44.3% which is 27% less product. Further decrease in the reaction time to 1 h caused almost 50% lower yield (Table 3). On the other hand, higher reaction durations of 4 h and 5 h resulted in higher yields of 64. 9% and 68.0%, respectively (Fig. 7-a). As a result, lower reaction durations can drastically affect the product yield; however, reaction time of 3 h or more do increase the product yield but the variation is not significant.

Table 3. Effect of changing the reaction time and temp. on 2,5-dibromo-p-xylene yield.

Reaction time (h)	Yield (%)	Reaction Temp. (°C)	Yield (%)
1	31.5	10	62.4
2	44.3	20	60.6
3	60.6	30	58.1
4	64.9	40	55.3
5	68.0	50	49.5

3.3. Variation of the reaction temperature

Changing the reaction temperature from 10°C to 50°C and its corresponding effect on 2,5-dibromo-p-xylene yield was also considered. In general, the overall change in the product yield obtained was not considerable over the specified range (Table 3). However, varying the reaction temperature had an inverse influence on the product yield, whereby higher reaction temperatures resulted in a slightly

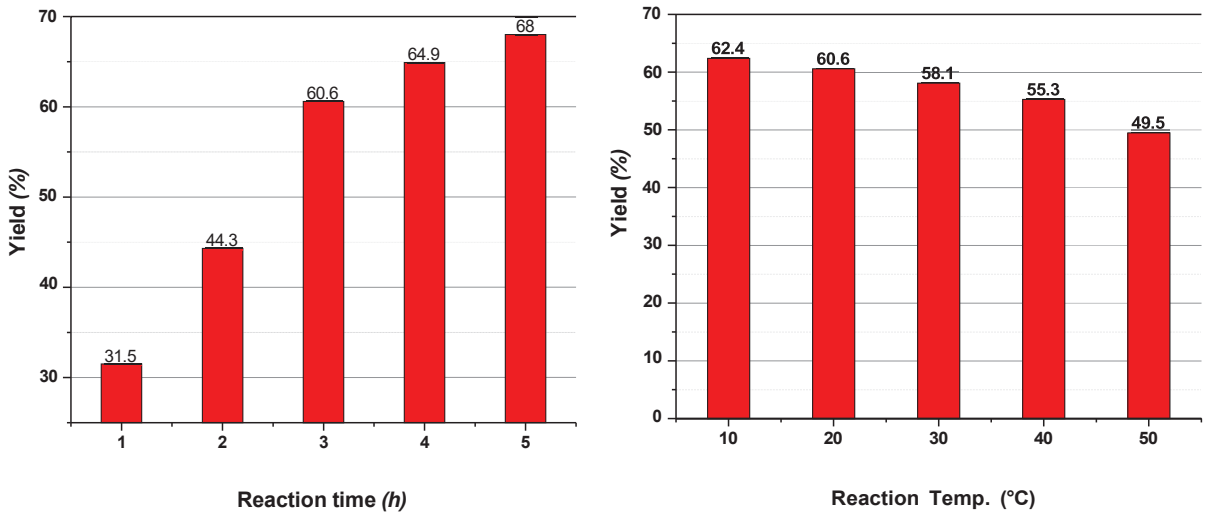

Figure 7. a) Effect of changing the reaction time on the 2,5-dibromo-p-xylene. b) Effect of reaction temperature on 2,5-dibromo-p-xylene.

lower yield and vice versa. Based on literature, the substitution reaction of bromine to the aromatic ring of p-xylene is an exothermic reaction. As a result, increasing the reaction temperature opposes the product formation (as witnessed in our case). Yet, the influence of the temperature is still minute compared to that of the bromine amount which agrees with our results (Fig. 7-b).

4. Conclusion

The bromination of p-xylene to produce 2,5-dibromo-p-xylene was successfully accomplished by varying the amounts of bromine, the reaction time, and the temperature. Our findings indicate that the optimal molar ratio for achieving the highest yield is 1:2 (p-xylene to bromine). An excessive quantity of bromine results in the formation of unwanted over-brominated byproducts. Additionally, the results demonstrate that an increase in reaction temperature slightly decreased the yield of 2,5-dibromo-p-xylene. The yield does not significantly increase beyond a reaction time of three hours. Noteworthy, the influence of temperature is relatively minor when compared to the variation in bromine amounts. In conclusion, this study illustrates that careful control of reaction parameters can effectively yield high-purity 2,5-dibromo-p-xylene, which holds potential for applications in the synthesis of metal- organic frameworks (MOFs) and other industrial processes.

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