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Oxidative bromination of non-activated aromatic compounds with AIBr₃/KNO₃ mixture

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Abstract

Bromination of non-activated aromatic compounds with reaction mixture containing KNO_3 and $AlBr_3$ was studied in liquid substrates and in solvent. Aluminium bromide has three different roles in this reaction mixture. First, it is a source of bromide ions, which are essential in oxidative bromination application. Second, it acts as a catalyst, and lastly, it forms acidic environment via its hydrolysis, which is necessary for enhancement of the oxidising properties of nitrate ions. It was shown that when changing the reaction conditions, different side reactions (like nitration or Friedel–Crafts type arylation) can occur. However, it is possible to guide the reaction path and receive the desired outcome by choosing the suitable reaction conditions. In addition, it was shown that there has to be water content in this reaction mixture as the bromine formation rate depends on it, while there exists an optimal volume of water, where bromine formation is the fastest.

Keywords Bromination of non-activated aromatics \cdot Oxidative bromination \cdot Lewis acid catalyst \cdot In situ bromine formation

Introduction

Brominated aromatics are valuable and widely used chemicals, which are usually prepared via electrophilic aromatic substitution reaction with molecular bromine (Bansal and Hyde 1998; Yoffe et al. 2013). Deut to the high toxicity of bromine and difficulties with handling it, many other methods have been developed for this purpose. Some of the alternative methods use bromo-organic compounds, such as *N*-bromosuccinimide (NBS) (Lambert et al. 1965; Duan et al. 1999; Tanemura et al. 2003; Prakash et al. 2004; Rajesh et al. 2007), sodium monobromoisocyanurate (SMBI) (Okada et al. 2003), dibromoisocyanuric acid (TBCA) (de Almeida et al. 2009) as bromination agents. Even though there is no need for Br₂ for aromatic

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Ida Rahu ida@ut.ee bromination, the bromine is still needed for synthesising these reagents. In addition, while using bromo-organic compounds, a large amount of strong acid (for example H_2SO_4) is often required (Gottardi 1969; Duan et al. 1999; Okada et al. 2003; de Almeida et al. 2009).

Another way to replace molecular bromine is to generate it in situ in the reaction mixture. In such methods, highly oxidative reagents such as bromates (Harrison et al. 1981; Groweiss 2000) or sodium periodate (Kumar et al. 2012) are frequently used. Unfortunately, this can bring along unwanted reactions and again, these methods also require strongly acidic environment. To overcome these limitations, there is a necessity for alternative bromination methods.

Recently, we have proposed that activated aromatic compounds can be brominated in the solid mixture of NaBr and KNO₃ as oxidising agent. This oxidative bromination method uses a relatively mild oxidizer, which diminishes the risk of side reactions. In addition, the used chemicals are considered eco-friendly (Rahu et al. 2018). However, as mentioned before, this method is not suitable for bromination of non-activated aromatics. To overcome this limitation, we suggested that the classically used Lewis acid catalyst AlBr₃ could be used in this reaction. Besides being a catalyst, AlBr₃ can also be the source for bromide ions, and thus replace NaBr in our proposed bromination method of

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activated aromatics. In this report, we studied the possibility to extend this in situ bromination method to non-activated and deactivated aromatics and optimised the reaction conditions to obtain the best outcome of the reaction.

Experimental

Starting materials and equipment

The starting materials NaBr, AlBr₃, KNO₃, acetanilide and bromobenzene were purchased from Reahim and benzene (Batch no.: PP/2011/00025) from Lach:ner. The purities of all substrates were verified by gas chromatography–mass spectrometry (GC–MS). The solvents hexane (Lot No. 8321S) and diethyl ether (Lot Nos.: STBG6864) were purchased from Sigma-Aldrich.

The scope of bromination reactions was assayed by analysing the reaction mixture using Agilent Technologies 7890A gas chromatograph with quadrupole mass spectrometer as the detector. In this study, nonpolar DB-5ms Ultra Inert column (phenyl arylene polymer virtually equivalent to 5% phenyl-methylpolysiloxane) with the radius of 250 μ m, film thickness of 0.25 μ m, and length of 30 m was used. The other gas chromatograph parameters were as follows: inlet split 20:1, 0.5 µL; carrier gas helium 6.0, flow rate 2 mL/ min, and pressure 25.548 psi. Detector ionisation energy was 70 eV, a transfer line and ion source temperatures were 280 °C and 230 °C, respectively. The scan rate of the used detector was 2 scans/s, the scanning range was 30-400 amu, the threshold was 20,000, and the reiteration number was 3. The GC-MS system was previously calibrated for acetanilide and its bromination product, and all respective data were corrected. To analyse the benzene bromination reaction, where three different dibrominated products formed, the standard substances (1,2-dibromobenzene, 1,3-dibromobenzene and 1,4-dibromobenzene) were used to distinguish between the isomers using their different retention times.

Two different temperature programs were used to assay the bromination reactions. The following temperature program was used to analyse the reaction mixture, when benzene or bromobenzene was used as substrate: 50 °C held for 4 min, followed by a temperature ramp of 10 °C/min to 200 °C, followed by 200 °C held for 5 min, giving a total program length of 24 min. When acetanilide was used as substrate, the temperature program was as follows: 140 °C held for 4 min, followed by a temperature ramp of 10 °C/min to 240 °C, giving a total program length of 14 min.

NMR spectra were recorded on a Bruker Avance III HD (operating at 700.1 MHz for ¹H spectra and 176.0 MHz for ¹³C spectra) at 25 °C in $CDCl_3$ (Lot No.: B15097, Sigma-Aldrich).

Bromination reactions without solvents

Liquid substrate (benzene or bromobenzene) was added to a 50-mL round bottom flask. In different experiments, the volume of substrate was 5 mL, 2.5 mL or 1 mL. Then, different amounts of oxidising agent KNO₃ (1.5 mmol, 2.5 mmol or 5 mmol) and anhydrous AlBr₃ as catalyst and bromine source (3.75 mmol, 7.5 mmol or 15 mmol) were added to the flask. The reaction mixture was stirred briefly. Then, the timing was started. Two minutes before stopping the reaction, the reaction mixture was stirred again. There was no constant stirring, because, as discussed in our previous work (Rahu et al. 2018), it has a perturbing effect to the bromine formation.

Reactions were stopped at different timepoints (15, 30, 60, 120 or 240 min) by adding 25 mL of saturated NaHCO₃ solution to remove unreacted AlBr₃ and neutralise the solution and 10 mL of Na₂S₂O₃ solution to be sure there is no excessive bromine in the reaction mixture. Then, 10 mL of diethyl ether was added, and the reaction mixture was stirred properly. Afterwards the organic layer was analysed by GC–MS. In preliminary experiments, where benzene was used as a substrate, an extra purification step was performed to separate main products (bromobenzene and nitrobenzene) to analyse them with NMR (see Supplementary data for spectrums).

Bromination reactions in solvent

1.5 mmol of substrate (acetanilide or benzene), 1.5 mmol of KNO_3 and 5 mL of hexane as a solvent were added to a 50-mL round bottom flask. Then, different volumes of water, as mentioned in the following discussion, were added as well. The reaction mixture was stirred thoroughly and then 7.5 mmol AlBr₃ was added and then the timing was started. The reactions were stopped as discussed earlier, but instead of 10 mL diethyl ether only 5 mL of diethyl ether was used. The organic layer was analysed by GC–MS. In the experiments, where acetanilide was used, the resultant bromination product was purified and analysed by NMR (see Supplementary data for spectrum).

Data analysis

When acetanilide was used as a substrate, all results are calculated and expressed as conversion values using peak areas from chromatograph:

$$Conversion(\%) = \frac{S_{product}}{S_{product} + S_{substrate}} \cdot 100\%,$$
(1)

where S_{product} is the peak area of *p*-bromoacetanilide, which was the only product detected in this system and $S_{\text{substrate}}$ showing the peak area of unreacted acetanilide.

In all other cases, the results are expressed as peak area ratios which were calculated as $S_{\text{product}}/S_{\text{substrate}}$, where S_{product} was the detected substance.

Sensitivity of GC–MS method used for this study depends on the particular molecule being measured. For the separate experiments, different amounts of products were detected, meaning the correct calculation of conversion values without thorough calibration of the machine would be practically impossible. Since the focus of this work is to show the trends, it was convenient to use peak area ratios.

Each experiment was carried out for at least three times and all results were averaged to minimise random variability.

Results and discussion

Suitability of studied reaction for bromination

In this reaction mixture (Scheme 1), bromination of aromatic compounds follows conventional electrophilic substitution mechanism, as discussed in our previous work (Rahu et al. 2018). All the results from current work are in good agreement with that, but some specific differences were noticed, which are discussed below.

For non-activated (even for slightly activated one like toluene) aromatics bromination with bromine, catalyst is needed because bromine itself as electrophile is not strong enough (Clayden et al. 2012). In this work, AlBr₃ as Lewis acid catalyst was chosen because it also acts as a source of bromide ions which are necessary in oxidative bromination method. Lewis acid catalyst forms complex with bromine, polarising the Br–Br bond, making it a stronger electrophile (Clayden et al. 2012). This complex cannot form in solid state and because of that, liquid substrates or solvents need to be used.

As shown in our previous work (Rahu et al. 2018), solvents have a great impact to the studied system as bromine formation depends directly on its choice. This is why only liquid substrates were used for investigating this advanced method.

Being a typical Lewis acid, AlBr₃ can give complexes with many functional groups which are present in the





substrate. To minimise the effects of the formation of such complexes on the results, benzene, which is nor activated or deactivated, and bromobenzene as a slightly deactivated aromatic compound, were chosen as model molecules.

In preliminary experiments when benzene was used as a substrate, it was found that bromination of non-activated aromatics is possible with this reaction mixture as bromobenzene formed. In addition, a tiny amount of nitrobenzene was also detected as a product, which is considered an unwanted side product. There have been earlier studies with similar reaction mixtures, where AlCl₃ was used instead of AlBr₃ with inorganic nitrates (Topchiev 1959; Olah et al. 1994). However, in most of the cases, only nitrated, not halogenated, aromatics were obtained.

We suppose that the reason for mostly halogenated product forming in our studied system is the fact that chlorine is a much stronger oxidising agent than bromine (Lide 2005) which means that the generation of chlorine from chloride ions requires a stronger oxidiser. In our system, a relatively mild oxidiser (nitrate ions) is used, so the formation of chlorine, which can halogenate the substrate, is impeded.

In addition, one should keep in mind that when nitrate ions are used as oxidisers, different nitrogen compounds can be formed. In our previous work (Rahu et al. 2018), we showed that in this reaction mixture, many nitrogen compounds are generated which means that in our system, the nitrating agent formation can be different from the one suggested by Olah et al. (1994) and the agent can be much less powerful.

Effect of the different reaction conditions to outcome

Based on the promising results from the preliminary experiments, the studied reaction mixture is suitable for bromination of non-activated aromatics. This was the reason for further studies of the reaction. Many experiments with different conditions were carried out to investigate whether it was possible to steer the outcome of the reaction to a certain result.

Effect of different substrate volumes

To start with, the amount of substrate in the reaction mixture was modified. Results obtained using benzene as a substrate are shown on Fig. 1. It can be seen that when smaller amount of substrate was used, more bromobenzene formed. On the other hand, it can be noted that the ratio of nitrobenzene was nearly constant during the experiments with similar conditions.

The smaller the amount of benzene was used, the larger the amount of side products formed. Beside formation of dibrominated products, biphenyl and 4-bromobiphenyl



Fig. 1 Bromination of different amounts (1, 2.5 and 5 mL) of benzene. Reactions were conducted using 1.5 mmol of KNO₃ and 7.5 mmol AlBr₃

were detected in these experiments. It is known from the literature (Smith 2013) that in acidic environment, two aromatic molecules are coupling, when treated with Lewis acid. The reaction is known as Scholl reaction. Previously, halogenated benzene coupling has been studied by Olah et al. (1962). It was found that fluorobenzene together with aluminium bromide gives fluorobiphenyl. However, with bromobenzene, bromobiphenyl was not detected, but they admitted that similar arylation definitely occured. This is why we suggest that bromobiphenyl is probably formed after bromination of biphenyl in our system. The fact that no bromobiphenyl was detected when bromobenzene was used as substrate (see Fig. 2.) confirms our assumption.

In bromobenzene bromination, like in benzene bromination when larger amount of substrate was used, a smaller amount of products was obtained. As expected, bromobenzene bromination is a slower reaction compared to benzene bromination. From Fig. 1, it can be seen that the amount of products stays nearly constant in time, but from Fig. 2, the amounts accumulate over time.

All three dibrominated isomers were received in bromobenzene bromination. The fact that benzene was detected as a product, is even more interesting. This indicates that bromination in this reaction occurs via a different mechanism than classical electrophilic substitution would be, or some other reactions can also occur. Halogenated benzenes isomerization in the presence of aluminium halide was



Fig. 2 Bromination of different amounts (1, 2.5 and 5 mL) of bromobenzene. Reactions were conducted using 1.5 mmol of KNO_3 and 7.5 mmol AlBr₃

studied by Olah et al. (1962). In their work, they found that bromobenzene isomerizes very easily when treated with aluminium bromide and it gives benzene and dibromobenzene as a result. They also noticed that after a longer time, metaisomer formed.

As it can be seen on Fig. 3, there were more nitrated products when smaller amounts of substrates were used. But in the separate experiments under constant conditions, nitrated product ratio to substrate stays almost the same, or decreases a little bit over time.

Effect of different nitrate and bromide amounts

From the previous chapter, while using smaller amounts of substrate, more side products were detected. To study the effect of the amounts of oxidiser and aluminium bromide used in the reaction, 5 mL of substrate was used.

When benzene was used as substrate, modifying amounts of oxidiser concluded that when larger amounts of oxidiser were used, more bromobenzene and nitrobenzene formed. In addition, a more dibrominated product was received (Fig. 4). The reason probably lies in the fact that bromine formation rate is higher when more oxidiser is used, as noted in our previous work (Rahu et al. 2018). However, the amount of oxidiser has no effect on the occurring side reactions which were described in the previous paragraph.

When bromobenzene was used as a substrate, using different amounts of nitrate had some noticeable effect only in case of shorter time range experiments. While using larger amounts of KNO₃, more products formed faster at the beginning of the reaction (see Fig. 5). The reason is supposedly again that bromine formation rate is higher in these conditions.

Like in previous experiments with bromobenzene, nitrated product ratio to substrate stays nearly constant during the studied time period (Fig. 6). In addition, in these experiments, more oxidiser means that more nitrated product is received.

For the next experiments, the amount of AlBr₃ used in the reaction mixture was varied. When 5 mL of substrate, 1.5 mmol KNO₃ and 15 mmol AlBr₃ were used, in experiments with benzene no nitration occurred. However, no effect on brominated product ratio was seen, compared to the experiments where 7.5 mmol of AlBr₃ was used in the same conditions. However, larger amount of AlBr₃ causes more side reactions, like biphenyl and 4-bromobiphenyl formation. When 3.75 mmol of AlBr₃ was used, almost the same results were received, like in experiment where 7.5 mmol AlBr₃ was used. When bromobenzene was the substrate, more AlBr₃ in the reaction mixture causes more nitrated product formation, but bromination process occurs faster. This can be easily explained by the fact that when bromobenzene is deactivated, its electrophilic substitution efficiency is related to the amount of catalyst used in the reaction.

Relying on the results observed in benzene bromination experiments, it can be concluded that bromine formation in this system must be a rapid process. In experiments in similar conditions, the bromobenzene ratio to benzene stays almost constant over studied time period.



Fig. 3 4-Nitrobromobenzene ratio to bromobenzene, in the experiment when different amounts (1, 2.5 and 5 mL) of bromobenzene were brominated. Reactions were conducted using 1.5 mmol of KNO_3 and 7.5 mmol $AlBr_3$



Fig. 4 Benzene bromination with different amounts (1.5, 2.5 and 5 mmol) of KNO_3 . Reactions were conducted using 5 mL of benzene and 7.5 mmol $AlBr_3$



Fig. 5 Bromobenzene bromination with different amounts (1.5, 2.5 and 5 mmol) of KNO_3 . Reactions were conducted using 5 mL of bromobenzene and 7.5 mmol AlBr₃

Oxidative bromination in solvent

To investigate the possibility of using this reaction mixture also in solvent, hexane was used. In preliminary experiments, 1.5 mmol of benzene and KNO₃, and 7.5 mmol of AlBr₃ were used in 5 mL of hexane. After 4 h only, benzene was detected. In addition, no characteristic colour of bromine could be seen. In our previous work (Rahu et al. 2018) with a similar reaction mixture, we found that no bromine forms in the absence of acid. As the used hexane was almost anhydrous, we suggested that not enough acid forms in the reaction mixture via AlBr₃ hydrolysis. Due to that, oxidising properties of nitrate ions were not strong enough. Importance of an acid can be shown directly with the reversible reaction equation, which represents molecular bromine formation from bromide ions, where nitrate ions are used as oxidising agents in acidic media (Lengyel et al. 1989):

$$NO_3^- + 2Br^- + 3H^+ \leftrightarrows Br_2 + HNO_2 + H_2O.$$
⁽²⁾

To check this hypothesis, different experiments where acetanilide as a model molecule which can be brominated easily, were conducted. In these experiments, different amounts of water were added into the reaction mixture. It was seen that when 500 μ L was added, more than 30% conversion value (see Fig. 7) was observed, meaning these



Fig. 6 4-Nitrobromobenzene ratio to bromobenzene in the experiments where different amounts (1.5, 2.5 and 5 mmol) of KNO₃ were used. Reactions were conducted using 5 mL of substrate and 7.5 mmol AlBr₃

conditions were optimal for the fastest bromine formation. It is important to notice that under these conditions, almost saturated KNO_3 solution was received. When 5 mL of water was added, no bromine formed in the reaction mixture.

A similar experiment was conducted with benzene and it could also be seen that more and larger amounts

of different products formed when 500 μ L of water was added. It is important to notice that under such conditions not all catalyst hydrolyse during the reaction, meaning there is enough residual to still act as catalyst (Fig. 8).

To conclude, this reaction mixture can be used in solvents, but one has to bear in mind that the dryness of the solvent is a very important component.



Fig.7 Acetanilide bromination in solvent, where different amounts of water were added. Reactions were conducted using 1.5 mmol of acetanilide and KNO_3 and 7.5 mmol AlBr₃ in 5 mL of hexane. The duration of the experiments was 15 min



Fig. 8 Benzene bromination in solvent where different amounts of water were added. Reactions were conducted using 1.5 mmol of benzene and KNO₃ and 7.5 mmol AlBr₃ in 5 mL of hexane. The duration of the experiments was 15 min

Conclusions

Bromination of non-activated aromatic compounds with and without solvent was observed using the reaction mixture of AlBr₃ and KNO₃. Besides the catalyst, aluminium bromide was also a source of bromide ions for in situ generation of bromine and its hydrolysis was used to form the necessary acidic environment. The main side reaction was aromatic nitration, but it was shown that the outcome of the reaction depends on the amounts of used substrate and reagents. By choosing suitable conditions for the experiment, it is possible to lead the reaction in the desired direction. The importance of water content used in the reaction mixture was also studied, and it was shown that there exists an optimal amount of water where the bromine formation occurs the fastest.

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Compliance with ethical standards

Conflict of interest The authors confirm that this article content has no conflict of interest.

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