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CHEMISTRY

Solvent-free synthesis of molecular bromine and its application for *in situ* bromination of aromatic compounds

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Abstract. Synthesis of molecular bromine in solvent-free reaction was studied using two different reaction mixtures. The first mixture consisted of solid KNO_3 and gaseous HBr, while the second setup used solid NaBr, KNO_3 and gaseous HCl. Bromine formation was determined through bromination reaction of acetanilide, added into the reaction mixture, and monitored by the gas chromatography–mass spectrometry (GC–MS). It was found that this solvent-free oxidative bromination technique could also be used for bromination of several other activated aromatic compounds but bromination of deactivated aromatics under the same condition was not successful, pointing to the need for a catalyst. The developed solvent-free bromination method for aromatics has several benefits as there is no need for heating, the oxidizing agent is mild, and product purification procedure is simple. All mentioned features make this process quite perspective for synthetic applications.

Key words: chemistry, bromination of aromatics, solvent-free reaction, *in situ* bromine formation, bromine assay.

1. INTRODUCTION

Classical aromatic bromination methods which use molecular bromine as reagent, have several disadvantages, foremost related to hazardous properties of Br_2. This issue has led to creation of various procedures where molecular bromine was generated *in situ* from bromide anion, which is environmentally much less harmful than molecular bromine [1–9]. However, for these methods efficient oxidizers are needed as the reduction potential of bromine is rather high [10]. Using strong oxidizers, in turn, may lead to oxidation of reaction substrates.

The second complication observed in the case of synthetic procedures, where bromine is generated *in situ*, is the selection of suitable solvents for this synthesis, as most aromatic bromination substrates as well as many oxidizers need to be solved in the reaction mixture. These circumstances call for additional steps of purification of the product, complicate the solvent reuse and increase the amount of waste formed in the overall process.

To address these limitations, solvent-free bromination methods that use tribromides [11–14] or bromination agents like N-bromosuccinimide [15,16], N,N,N',N'-tetrabromobenzene-1,3-disulfonamide, poly(N,N'-dibromo-N-ethylene-benzene-1,3-disulfonamide) [17] or strong oxidizer like oxone [18] have been implemented. As the listed reagents have rather complex structures and are expensive, these methods also do not meet the basic requirements of sustainability [19].

In this study, a solvent-free reaction is described, where molecular bromine is synthesized using a mild oxidizing agent KNO_3 from gaseous HBr. The molecular bromine, formed in this solvent-free reaction mixture, can be used for bromination of aromatic compounds and added into the reaction mixture as bromination substrates. It is found that the yield of the bromination reaction depends upon the structure of the bromination substrate and is relatively high in the case of activated aromatics.

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A similar solvent-free reaction system that contains the mixture of solid KNO_3 and NaBr, where bromine formation was induced by gaseous hydrogen chloride, was also described and used for bromination of aromatics. Some features of these two reaction mixtures are compared and their applicability for bromination of aromatic compounds is discussed.

2. MATERIALS AND METHODS

2.1. General

Starting materials NaBr, KNO_3, acetanilide, and bromobenzene of the highest grade of purity available were from Reahim (former USSR), 4-hydroxy-3-methoxybenzaldehyde and 1,3-dimethoxybenzene from Sigma–Aldrich, 1-bromo-2,4-dimethoxybenzene from Aldrich, benzene and toluene from Lach:ner. Dry NaBr and KNO_3 samples were obtained by drying these salts in oven and storing in desiccator using anhydrous $MgSO_4$ as desiccant. Diethyl ether was purchased from Sigma–Aldrich and was used without additional purification. The purity of bromination substrates was verified by gas chromatography–mass spectrometry (GC–MS) as described below. In addition, purity of acetanilide was verified by nuclear magnetic resonance (NMR) spectroscopy (^{1}H NMR (700.1 MHz, $CDCl_3$): δ 7.550 (s, NH), 7.50 (d, 2H, J = 7.7 Hz, Ar(H)), 7.31 (t, 2H, J = 7.7 Hz, Ar(H)), 7.10 (t, 1H, J = 7.4 Hz, Ar(H)), 2.17 (s, 3H, CH_3); ^{13}C NMR (176.0 MHz, $CDCl_3$): δ 168.7, 138.0, 129.1, 124.5, 120.1, 24.7). The melting point of this compound was 115 ± 1 °C (lit. mp 114.3 °C [20]).

GC–MS analysis were performed using an Agilent 7890A gas chromatograph (Agilent Technologies) equipped with a nonpolar DB-5ms Ultra Inert column (phenyl arylene polymer virtually equivalent to 5% phenyl-methylpolysiloxane) with the length of 30 m, radius of 0.25 mm, and film thickness of 0.25 μm (inlet split 20:1, 0.5 μL; carrier gas helium 6.0, flow rate 2 mL/min, pressure 26.561 psi). The chromatograph was equipped with a quadrupole mass spectrometer (QMS) as the detector, using electron ionization energy of 70 eV, transfer line temperature of 280 °C, ion source temperature of 230 °C, scanning range of 30–400 amu, threshold of 20 000, reiteration number of 3, and a detector scan rate of 2 scans/second. The GC–MS system was calibrated considering the different ionization degrees of the reaction substrate and product, and all relevant data were corrected. The following temperature program was used to analyse the acetanilide, 4-hydroxy-3-methoxybenzaldehyde, and 1-bromo-2,4-dimethoxybenzene bromination products: 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. In all other cases, the temperature program was different: 50 °C held for 4 min, followed by a temperature ramp of 10 °C/min to 240 °C, followed by 240 °C held for 5 min, giving a total program length of 28 min.

NMR spectra were recorded on a Bruker Avance III HD (operating at 700.1 MHz for ^{1}H spectra and 176.0 MHz for ^{13}C spectra) at 25 °C in $CDCl_3$ (Sigma–Aldrich), using solvent residual signal as internal reference.

2.2. Gaseous hydrogen halides

Hydrogen chloride was prepared by adding concentrated sulfuric acid to solid NaCl and heating the mixture, and directed through concentrated H_2SO_4 for drying. The gas flow rate was controlled by counting the HCl bubbles in sulfuric acid.

Dry hydrogen bromide was produced in a reaction between acetyl bromide and anhydrous 2-methylpropan-1-ol. Acetyl bromide was added into a two-neck round-bottom flask, placed into a water/ice cooling bath with magnetic stirrer. Top neck was attached with pressure equalizing dropping funnel and side neck with reflux condenser, which was connected with the reaction flask where bromination occurred. 2-methylpropan-1-ol was added dropwise to acetyl bromide via the dropping funnel. After all substance was added, the cooling bath was removed. HBr was dissolved in the formed ester and by heating this solution it was possible to generate dry hydrogen bromide flow, which flow rate can be controlled by changing heating intensity.

2.3. Reactions

Reactions with HBr were performed in 50 mL flasks, which were connected with the source of dry hydrogen halide and contained different amounts of solid KNO_3 (1.1, 2.75, 5.5 mmol or 11 mmol) as well as the bromination substrate (1, 5 or 10 mmol). The reaction was initiated by directing the gas into the vessel and keeping its flow rate the same during the reaction. The reaction was stopped at the appropriate time moments by adding 20 mL of saturated $NaHCO_3$ solution into the flask and the excess Br_2 was removed by adding 10 mL of $Na_2S_2O_3$. Then 5 mL of diethyl ether was added and the organic layer was analysed by GC–MS for determination of the remaining substrate and the bromination reaction products. Different reaction times were used as mentioned in the following discussion.

Reactions with HCl were performed in the similar way with 1.1 mmol KNO_3, 1.1 mmol NaBr, and 1 mmol acetanilide as bromination substrate in the reaction flask. The process was initiated by directing HCl into the reaction vessel and keeping the gas flow permanent. At appropriate

time moments (see Results and Discussion), the reaction was terminated as described above, and the organic layer was analysed by GC–MS for detection of the reaction products as well as the remaining initial compound.

Structure of the reaction product, *p*-bromoacetanilide, was verified by NMR analysis, yielding ^{1}H NMR (700.1 MHz, $CDCl_3$): δ 7.43–7.39 (m, 4H, Ar(H)), 7.23 (s, 1H, NH), 2.17 (s, 3H); ^{13}C NMR (176.0 MHz, $CDCl_3$): δ 168.4, 137.1, 132.1, 121.5, 117.0, 24.8.

2.4. Data analysis

The chromatograms obtained from GC–MS measurements were integrated and the conversion values were calculated as follows:

$$Conversion\ (\%) = \frac{S_{product}}{S_{sum}}, \quad (1)$$

where $S_{product}$ is the peak area of the product and S_{sum} represents the sum of peak areas for the product and remaining substrate.

When acetanilide was used as substrate

$$S_{sum} = S_{acetanilide} + S_{p\text{-}bromoacetanilide}. \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Molecular bromine formation

The initial step of the reaction of gaseous HBr with solid KNO_3 can be presented by the following equation:

$$2\ HBr + KNO_3 \rightarrow KNO_2 + Br_2 + H_2O. \quad (3)$$

However, it is important to mention that nitrites are also oxidizing agents [10,21], and moreover, a cascade of other oxidizing nitrogen compounds can be formed in this process [21]. Consequently, the consumption of the oxidizer should not follow the stoichiometry, predicted by the reaction (3), and this explains some results of this study. Secondly, as the continuous and similar flow of HBr was applied at normal pressure throughout all studies, the concentration of this reagent was constant in all experiments. These aspects simplify understanding of the kinetics of the bromination reaction.

The bromine formation was qualitatively observed by colour change in the reaction vessel, first-hand on the surface of the solid salt. As no convenient and rapid method for direct determination of bromine was available, this process was investigated indirectly by monitoring bromination of acetanilide which was added into the reaction mixture for the assay purposes

$$acetanilide + Br_2 \rightarrow p\text{-bromoacetanilide} + HBr. \quad (4)$$

To confirm that this analytical procedure is suitable for bromine formation monitoring, the initial phase of the reaction was studied using various amounts of KNO_3 and acetanilide. Results of these experiments are shown in Figs 1 and 2.

It can be seen in Fig. 1 that the conversion of acetanilide into its brominated derivative is proportional to the amount of the oxidizer. Therefore, it can be concluded that the initial rate of the bromination reaction, which in turn, depends on bromine formation, is controlled by the amount of oxidizer. More precise quantification of the effect is complicated by the presence

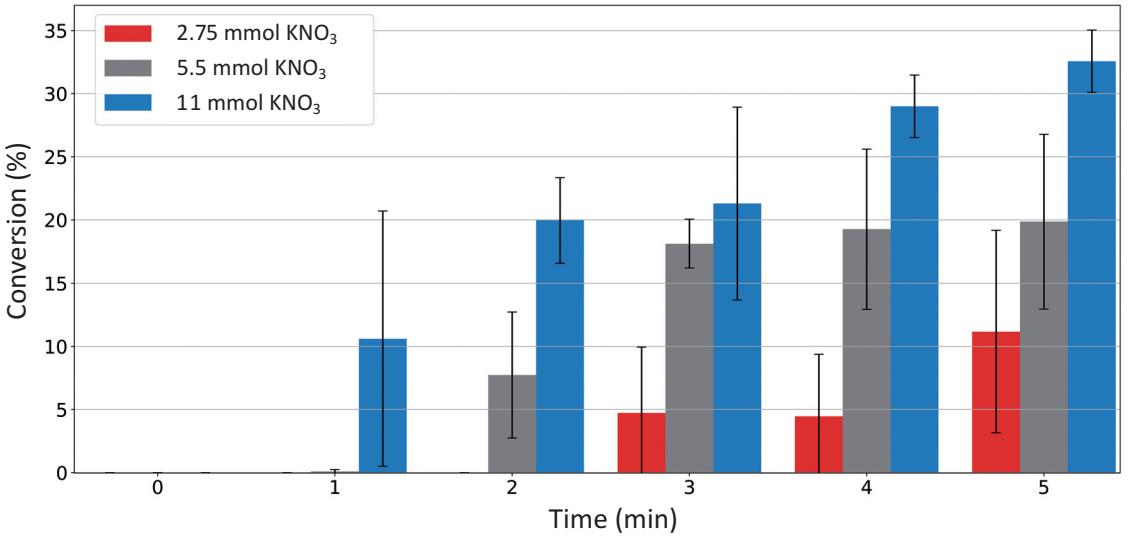

Fig. 1. Results of acetanilide oxidative bromination in the reaction system, containing different amounts of KNO_3 (2.75, 5.5 or 11 mmol), 5 mmol of acetanilide and at continuous flow of gaseous HBr. The error bars were calculated from triplicate experiments.

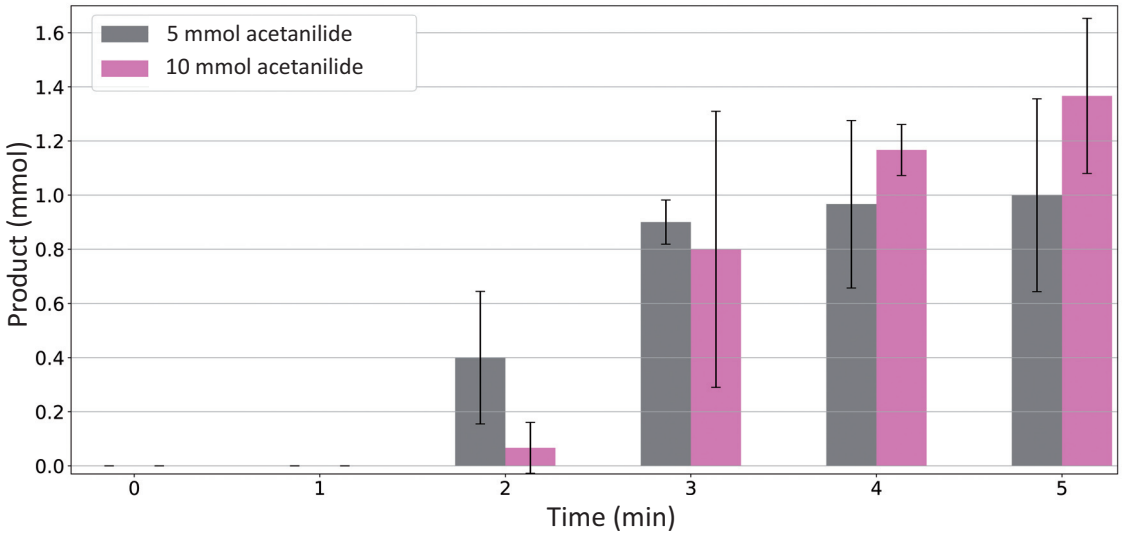

Fig. 2. Bromination of different initial amounts (5 or 10 mmol) of acetanilide in the presence of 5.5 mmol KNO_3 and at continuous flow of gaseous HBr. The error bars were calculated from triplicate experiments.

of lag period which can be observed in the beginning of the reaction (Fig. 1).

In the next series of experiments, influence of different amounts of acetanilide on the initial phase of the bromination reaction was studied. The results of these experiments are shown in Fig. 2. It can be seen that the increase in acetanilide amount from 5 to 10 mmol at constant amount of KNO_3 (5.5 mmol) has no influence on formation of the bromination product. Therefore, it can be concluded that acetanilide bromination occurs fast, if compared with the reaction of bromine formation, and this reaction can be used for bromine assay in the solvent-free conditions. The same conclusion was previously made for bromine formation reaction in some organic solvents [22]. However, in both cases, some excess of bromination substrate must be used to obtain meaningful results of the assay.

In a separate series of experiments, similar solvent-free bromine formation reaction was investigated using the mixture of solid NaBr and KNO_3 in the atmosphere of HCl. It is known that gaseous HCl rapidly exchanges bromide ions in solid sodium bromide, leading to the formation of HBr [23]:

$$\mathrm{HCl(g) + Br^-(NaBr\ surface)} \leftrightarrows \mathrm{HBr(g) + Cl^-(NaBr\ surface)}. \quad (5)$$

This makes the replacement of HBr with NaBr possible. The experiments where the mixture of NaBr (1.1 mmol) and KNO_3 (1.1 mmol) was used for acetanilide bromination in the presence of gaseous HCl, were performed during 15 min, and the results of these runs are brought out in Table 1. This table also includes results of other experiments, where HBr and the same amount of KNO_3 but also HBr, NaBr and KNO_3 were used. It can be seen that similar conversion values were obtained in these three experiments, demonstrating that NaBr can be used for bromine synthesis despite the absence of solvents. Secondly, these results also confirm the conclusion that hydrogen bromide acts as the bromine source in all these reactions of molecular bromine formation. On the other hand, if these reaction mixtures are compared from the point of view of synthetic application, the usage of solid KNO_3 and gaseous HBr is preferable. This is because minor amounts of chlorinated aromatic compounds were detected even in acetanilide bromination experiments in the presence of HCl. Therefore, the simplest reaction mixture, including KNO_3 and HBr, was used in all subsequent experiments.

Table 1. Acetanilide bromination in the reaction mixture containing solid KNO_3 (1.1 mmol), NaBr (1.1 mmol), acetanilide (1 mmol), under the continuous flow of HBr or HCl (normal pressure, 25 °C). Each experiment lasted 15 min. Results of triplicate measurements are listed

Reactants	Conversion (%)
NaBr (s) 1.1 mmol; KNO_3 (s) 1.1 mmol; HCl (g)	25 ± 3
NaBr (s) 1.1 mmol; KNO_3 (s) 1.1 mmol; HBr (g)	28 ± 1
KNO_3 (s) 1.1 mmol; HBr (g)	29 ± 2

3.2. Acetanilide bromination

The reaction of acetanilide bromination was monitored during several hours and the summary of these results, obtained with initial KNO_3 and acetanilide amounts of 5.5 and 5 mmol, respectively, is shown in Fig. 3. It can be seen that the amount of *p*-bromoacetanilide in the reaction mixture increased progressively, until the complete conversion was achieved in about four hours. Taking into consideration the results shown in Fig. 1, it can be suggested that this reaction time can be shortened by using larger initial amounts of KNO_3. This could be an important option in the case of synthetic implication of this procedure.

3.3. Bromination of other aromatics

Bromination of several aromatic compounds was tested using the described solvent-free bromination system, and the results of these experiments are listed in Table 2. It can be seen that this substitution reaction goes well with compounds possessing activated aromatic ring. By analogy with acetanilide, complete bromination of vanillin was

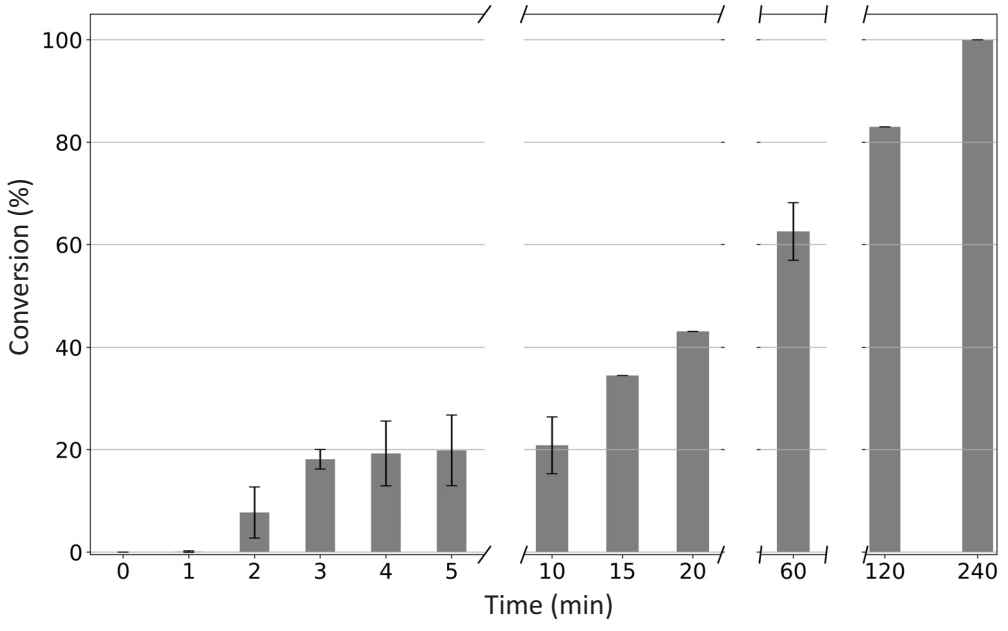

Fig. 3. Acetanilide bromination in the reaction mixture, containing 5.5 mmol KNO_3 and 5 mmol acetanilide, and at constant HBr flow (normal pressure). The error bars were calculated from triplicate experiments, while conversion values at 15, 20 and 120 min were calculated from single experiments.

Table 2. Bromination experiments with activated and deactivated aromatic compounds using the solvent free bromination method. Reactions were conducted using 5 mmol of bromination substrate, 11 mmol of KNO_3 and at constant flow of HBr

Substrate	Reaction time (min)	Product detected	Conversion (%)
N-phenylacetamide (acetanilide)	60	4-bromoacetanilide	100
4-hydoxy-3-methoxybenzaldehyde (vanillin)	60	5-bromo-4-hydroxy-3-methoxybenzaldehyde	100
1,3-dimethoxybenzene	60	1-bromo-2,4-dimethoxybenzene	74
		1,5-dibromo-2,4-dimethoxybenzene	16
1-bromo-2,4-dimethoxybenzene	240	1,5-dibromo-2,4-dimethoxybenzene	50
toluene	240	*p*-bromotoluene	≤ 3
		o-bromotoluene	≤ 2
benzene	240	–	0
bromobenzene	240	–	0
benzaldehyde	240	–	0
benzoic acid	240	–	0

observed during 1 h, when 11 mmol of KNO_3 was used in the reaction mixture. When 1,3-dimethoxybenzene was used as substrate, formation of mono- and dibrominated products was observed. At the same time, only low conversion of 1-bromo-2,4-dimethoxybenzene into its brominated derivative was observed under the same reaction conditions. Moreover, the slightly activated toluene was practically not brominated, while in the case of benzene and deactivated aromatics like bromobenzene, benzaldehyde and benzoic acid, no formation of the bromination products was observed during 4 h. These results agree with the suggestion that the studied bromination reaction follows the classical mechanism of electrophilic aromatic substitution, where the participation of strong Lewis acids as catalysts is needed in the case of deactivated aromatic compounds. Therefore, amendment of the described minimal reaction system of *in situ* bromination with catalyst could be an interesting challenge.

It is important to emphasize that the proposed solvent-free bromination procedure allows simple product purification, especially if the formation of by-products can be minimized or completely avoided. Therefore, after work-up of the crude product with aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ for removal of bromine excess and neutralizing the reaction mixture, the reaction product can be easily extracted and recrystallized. The yields of the final products depend on the effectiveness of product processing procedures. In our experiments, the yield of the crude bromination product was 91% for acetanilide and 90% for vanillin.

4. CONCLUSIONS

The absence of solvent in the proposed bromination reaction mixture significantly reduces the amount of waste compared to all conventional bromination methods. Moreover, from the point of sustainability of the synthesis, it is important to emphasize that in this oxidative bromination reaction the bromine atom efficiency may approach 100%, while in the reaction with molecular bromine the bromine atom efficiency is only 50%. Furthermore, in the proposed solvent-free system, mild solid oxidizing agent KNO_3 is used. The relatively moderate oxidizing properties of this reagent minimize the role of possible oxidative side-reactions and allow simple and straightforward purification of the reaction products. Also, the synthesis does not require heating that further minimizes the complexity of the procedure set-up. As the bromine formation rate can be effectively modulated by variation of the amount of KNO_3 in the reaction mixture, it is possible to control kinetics of the bromination reaction that is an important advantage and allows bromination of reactive compounds with good selectivity. All these factors result in high conversion values when the method is used for *in situ* bromination of activated aromatic compounds.

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Molekulaarse broomi süntees lahustivabades tingimustes ja selle kasutamine aromaatsete ühendite *in situ* broomimiseks

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Töös uuriti molekulaarse broomi sünteesi lahustivabades tingimustes. Selleks kasutati kaht erinevat reaktsioonisegu. Esimene segu koosnes tahkest KNO_3-st ja gaasilisest HBr-st, teises reaktsioonisegus kasutati tahket NaBr, KNO_3 ning gaasilist HCl. Broomi teket uuriti reaktsioonisegusse lisatud atseetaniliidi broomimisreaktsiooni abil, mille ajalist toimumist jälgiti gaasikromatograafilist analüüsi kasutades.

Selliselt täpsustati molekulaarse broomi tekkereaktsiooni tingimusi ja seaduspärasusi. Leiti, et antud lahustivabades tingimustes toimuvat broomi sünteesi saab edukalt kasutada aktiveeritud aromaatse tuumaga ühendite broomimiseks *in situ* tingimustes. Benseeni ja desaktiveeritud aromaatsete ühendite broomimiseks antud meetod aga ei sobi ning vajab täiustamist katalüsaatori lisamisega. Töös näidati, et lahustivabal aromaatsete ühendite broomimismeetodil on klassikaliste sünteesimeetodite ees mitmeid eeliseid, näiteks puudub vajadus reaktsioonisegu kuumutamiseks ja kasutatakse mõõduka tugevusega oksüdeerijat, mis vähendab oluliselt kõrvalreaktsioonide toimumise võimalust. Samuti on broomitud produkti eraldamine reaktsioonisegust ja järgnev puhastamine võrdlemisi kerge. Kirjeldatud asjaolud muudavad antud solvendivaba molekulaarse broomi sünteesimeetodi ja selle kasutamise aromaatsete ühendite broomimiseks perspektiivikaks võimalike tehnoloogiliste rakenduste seisukohast.