

FINAL REPORT

Continuous Solventless Photochemical Nitration Using Nitrogen Dioxide

SERDP Project WP-2751

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TNO - Defence, Security and Safety

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The objective of this research was to avoid the use of any solvent and the liquid nitration acids, by switching to the gas phase nitration agent using NO2. Nitrogen dioxide can be activated by irradiation with light of specific wavelengths and will subsequently attack the moiety of the compound in question to convert it into its nitro analogue. In a light reactor, this reaction is executed and can be augmented by the addition of a solid catalyst.

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solvent, solventless, nitration acid, nitrogen dioxide, light reactor, NTO, fluidized bed, benzene, toluene

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List of Acronyms

| | |
|------------|---|
| (ATR)-FTIR | (Attenuated Total Reflectance) - Fourier Transform InfraRed |
| DMSO | DiMethyl Sulfoxide |
| EU | European Union |
| FP | Framework Program |
| GC-MS | Gas Chromatography – Mass Spectrometry |
| LED | Light Emitting Diode |
| NMR | Nuclear Magnetic Resonance |
| NTO | 3-nitro-1,2,4-triazole-5-one |
| SEED | SERDP Exploratory Development |
| SERDP | Strategic Environmental Research and Development Program |
| TNO | Netherlands Organization for Applied Scientific Research |
| TO | 1,2,4-triazole-5-one |
| UV-VIS | UltraViolet – Visible (range) |
| WP | Weapon Systems and Platforms |
| ZSM-5 | Zeolite Socony Mobil-5 |

Keywords

Nitration, benzene, nitrobenzene, UV-VIS, light reactor, 1,2,4-triazole-5-one (TO), 3-nitro-1,2,4-triazole-5-one (NTO), catalysis, fluidization, microwave radiation

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Executive Summary

The objective of this research is to avoid the use of any solvent and the liquid nitration acids, by switching to the gas phase nitration agent using NO₂. Nitrogen dioxide can be activated by irradiation with light of specific wavelengths and will subsequently attack the moiety of the compound in question to convert it into its nitro analogue. In a light reactor, this reaction is executed and can be augmented by the addition of a solid catalyst. To test the reactor system to the extreme, a solid – gas reaction was executed in the reactor by converting 1,2,4-triazole-5-one (TO) to 3-nitro-1,2,4-triazole-5-one (NTO). This was achieved by using nitrogen dioxide as the fluidizing agent, activating the nitration reaction by supplying light to the reactor. Where appropriate a catalyst was added to enhance the yield of NTO and to reduce the reaction time. It was experimentally determined that the enhancement of the nitration reaction with microwaves had no discernable effect on the yield and products formed.

The nitration of benzene with nitrogen dioxide under the influence of light was successfully shown and yields of up to close to 100% nitrobenzene were demonstrated. For this the most ideal ratios of substrate, nitrogen dioxide and oxygen were established. The time needed for reaching such yields is too high (up to two hours). It was shown that the application of catalysts can significantly reduce the reaction time needed to achieve the same yields in a matter of minutes. This means that a sound business case for a continuous process seems to be achievable.

The nitration of a solid material, 1,2,4-triazole-5-one (TO), with nitrogen dioxide in a fluidized bed has been successfully demonstrated, albeit the yields found for nitro-1,2,4-triazole-5-one (NTO) were low. This was predominantly due to the morphology of NTO, which can be best described as pancake-like. Due to unfavorable particle shape, the fluidization of TO was troublesome, resulting in low yields of NTO.

It was found that the application of microwave radiation on the nitration reaction (both the gas phase nitration of benzene to nitrobenzene as well as the nitration of TO to NTO) did not have a discernable influence.

1 Introduction

1.1 Objective

The proposal contributes to the reduction/minimization of acid mixtures and hence waste streams, avoiding the use of solvents which could be contaminated, and be considered as a waste stream. This will also minimize the post processing process (e.g. purification) of the product (reduce energy consumption). This is achieved by the continuous solventless photochemical nitration using nitrogen dioxide.

1.2 Background

Gas phase nitrations are well documented in literature. Generally, the nitrating agent is nitric acid, nitrogen dioxide or the combination of nitrogen dioxide with ozone [1]. In most cases, benzene or toluene is used as the substrate to be nitrated and the final product is generally selectively mono-nitrated [1]. From a safety point of view, as well as the consideration of minimizing the complexity during the scaling up of the reaction, the combination of nitrogen dioxide and ozone is not considered further in this proposal. Although ozone can be made in situ to reduce the adverse effects of working with this reactive material, for larger scale systems the other two gas phase systems are deemed more straightforward.

Using nitrogen dioxide as the nitrating agent, most of the published work either uses photochemical activation of the nitrogen dioxide or a catalyst to aid the nitration reaction. Watanabe et al. [2] investigated the mono-nitration of benzene using a high-pressure mercury lamp as the photochemical initiator in a batch reactor at room temperature and atmospheric pressure. Although the yield of nitrobenzene was low (20-30%) for the direct reaction of nitrogen dioxide with benzene, the selectivity of the reaction was close to 100%. It was found that the addition of oxygen to the system increased the yield significantly to 80+%, while the selectivity was not significantly affected. It should be noted that the spectral output of the mercury lamp is broad, and as such, the photonic quantum yield is low (amount of energy effectively used for the reaction compared to the total spectral output). Bunbury [3], on the other hand, acknowledged the specific wavelengths at which nitrogen dioxide is either dissociated or activated, and showed that the concentration ratio of benzene to nitrogen dioxide, as well as temperature (10 – 100 °C) are crucial processing parameters for obtaining the highest yield of nitrobenzene.

Kirkby [4] used the zeolite NaZSM-5 as a catalyst for the nitration of chlorobenzene to exclusively yield para-chloronitrobenzene using nitrogen dioxide as the nitrating agent. The nitration reaction is understood to be the combined action of NO₂, N₂O₄ and N₂O₅, the latter two being produced in situ by the catalyst as detected by FTIR. Temperature was seen to be a crucial parameter, as an increase in temperature leads to an enhanced reaction rate, while reducing the yield due to the desorption of nitrogen dioxide from the catalyst surface. Owsley and Bloomfield [5] used commercial molecular sieves as catalyst in the conversion of chlorobenzene to the mono-nitrated para- and ortho- equivalents in a flowing system. Yields were generally low (20 – 40%) and the selectivity generally in the order of 40 – 60% para-chloronitrobenzene.

Lee and Albright [6], without any photochemical activation, carried out the nitration of cyclohexane with nitrogen dioxide at high temperatures (200 – 260 °C) and saw a range of

nitrated and oxidized products being produced as well as charred material. It was found that temperature, concentration ratio of cyclohexane to nitrogen dioxide, residence time and potentially surface material of the reactor affected the yield and selectivity of the reaction. Kumar et al. [7] published a patent in which polymers were nitrated using nitrogen dioxide in a fluidized bed, using nitrogen dioxide at elevated temperatures (60 – 140 °C). Oxygen is added to the system to enhance the conversion rate. Similarly, photochemical initiation was not used. Wang [8] patented a process using nitrogen dioxide to nitrate alkenes uncatalyzed and without light activation, in the gas phase at elevated pressures (up to 12 bars) and temperatures ranging between 250 – 350 °C. The conversion was aided by adding oxygen to the system. When nitric acid vapor is used as the nitrating agent, the academic focus is almost exclusively on the development of suitable solid superacid catalysts. Brei et al. [9] developed a catalyst based on WO_3/ZrO_2 and studied the yield and selectivity at atmospheric pressure and a temperature of 170 °C for the nitration reaction of benzene in a flow cell. The concentration ratio of benzene to nitric acid is once again a crucial parameter. The selectivity was 99.8% and the yields varied between 65 – 80%. Koskin et al. [10] developed a catalyst based on sulfated perfluoropolymers (Nafion) supported on carbon nanofibers,. Reactions were performed at 160 – 170 °C, at atmospheric pressure. It was shown that the catalyst degraded as a function of time. Selectivity of converting benzene to nitrobenzene was 99.9%. Kozlova et al. [11] used a wide range of natural and synthetic aluminosilicates for the conversion of benzene to nitrobenzene. It was found that increasing the temperature to 150 °C increased the selectivity and yield of the reaction.

Kuznetsova et al. [12] also used the zeolite ZSM-5 for the conversion of benzene to nitrobenzene at atmospheric pressure and temperatures in the range of 140 – 170 °C. The addition of oxygen to the system decreased the yield of nitrobenzene. As the temperature increased beyond 140 °C, side products like carbon monoxide and carbon dioxide were formed, as well as nitrophenols. Dongare et al. [13] patented a process for the conversion of benzene with nitric acid over molybdenum silica catalysts. The selectivity was in the range of 98 – 100% and the yield was between 50 and 75% at temperatures between 120 – 180 °C. Toops et al. [14] patented a pure gas phase process for the conversion of predominantly alkanes to the corresponding nitroalkane analogues at temperatures up to 600 °C and pressures up to roughly 10 bar. Yields were poor (10%).

1.3 Prior knowledge

With the EU FP7 project CyclicCO₂R [15], in which TNO participated, the goal was to produce cyclic carbonates by reacting, for instance, glycol or an epoxide with carbon dioxide. Carbon dioxide was used as a feedstock. The ultimate goal was to find ways to reduce the carbon dioxide concentration in the atmosphere and treating carbon dioxide as a valuable reactant instead of considering it a waste product. The project had several work packages and one work package was a high risk – high gain attempt to only use carbon dioxide and water as feedstock to make the corresponding carbonates. In essence, this meant producing ethylene by electrochemically coupling two carbon dioxide molecules and subsequently, oxidizing the ethylene to ethylene oxide with water, using a photochemical approach. The produced ethylene oxide can then be used to make the cyclic carbonate by reacting it with, once again, a carbon dioxide molecule. From the onset, it was of paramount importance that the carbon dioxide balance of all these reactions should be positive, i.e., the number of carbon dioxide molecules used in the reactions to make the carbonate should be less than the number of carbon dioxide molecules produced during the processing itself. As such, the choice is made for renewable energy sources (wind, solar) to enable the reactions to proceed electro- and/or photochemically.

A further, highly ambitious goal was the ability to use this principle, for instance on Mars, to make useful materials at distant locations with only electricity, light, carbon dioxide and water at hand.

For the photochemical conversion of ethylene to ethylene oxide, a custom made continuous flow reactor was built by TNO to enable this conversion. Details of this reactor are given in section 2. The reactor enabled the continuous feeding of ethylene and water vapor, mixed at molecular level, while in contact with the catalyst deposited on the sapphire rods inside the reactor. The photocatalyst absorbed the photons, activating the reaction between ethylene and water. In the end, the electrochemical reactor was feeding the photochemical reactor with ethylene to produce ethylene oxide directly from carbon dioxide.

1.4 Approach

The objective of this research is to avoid the use of any solvent and the liquid nitration acids, by switching to a gas phase nitration agent using NO₂ or nitric acid in the gas phase. The nitrogen dioxide can be activated by irradiation with light of specific wavelengths and will subsequently attack the moiety of the compound in question to convert it to its nitro analogue. In a light reactor, this reaction is executed and can be augmented by the addition of a solid catalyst, deposited in a thin layer on the light rods present in the reactor. When needed, the nitration reaction can be further enhanced by also applying microwaves in the same reactor system. To test the reactor system to the extreme, a solid – gas reaction will be executed in the reactor by converting 1,2,4-triazole-5-one (TO) to 3-nitro-1,2,4-triazole-5-one (NTO). This is achieved by using nitrogen dioxide as the fluidizing agent, activating the nitration reaction by supplying light to the reactor.

If successful, the reactor will neither require liquid acid mixtures for nitration purposes nor solvents for facilitating the reaction, hereby minimizing the waste streams significantly. The reactor will in that case be highly flexible to nitrate almost any compound regardless of the state of the substance (gas, liquid, solid) and is modular in nature, enabling adjustment of the output at any given moment in time.

The project is divided into the following tasks:

- Task 1: Validation of the light reactor. After completion of WP 1, it is expected that the selectivity will be close to 100% and the yield will be in the order of 80 – 90%.
- Task 2: Photocatalytic improvement of yield using light reactor. To increase the yield in the next step, the sapphire rods will be coated with a catalyst known in literature to assess if this enhances the yield and selectivity of the nitration process in combination with the photochemical activation of the nitrogen oxide as observed in WP1. The combined results of WP1 and WP2 will indicate whether the photochemical or photocatalytic route is economically more interesting. If the degradation and erosion of the catalyst is low or absent, the process of placing the catalyst on the glass rods will be straightforward, and the yield will be significantly enhanced. The photocatalytic route will thus be preferred. With selectivity and yield close to 100%, the post processing effort will be minimal. Subsequently, the validated reactor concept will be used for the nitration of 1,2,4-triazole-5-one (TO) to 3-nitro-1,2,4-triazole-5-one (NTO). As the precursor is a solid material at room temperature, the complexity of the reaction increases. The previous work packages considered a pure gas phase reaction and with TO, this is changed to a gas-solid reaction scheme. The two-phase system will make

mixing on a molecular level, difficult to impossible, and requires deep penetration of the nitrating agent.

- Task 3: Photochemical/catalytic conversion of TO to NTO. Should the yield of NTO be low, the light reactor can be modified to also incorporate a microwave source. For this purpose, the metal housing of the reactor will be replaced by either a glass or ceramic version. The microwave source will be clamped around the reactor housing. In this instance, the nitrogen dioxide is thus activated using the glass rods from the inside of the reactor, and the reactivity of TO is stimulated using microwaves.
- Task 4: Microwave enhanced photochemical conversion of TO to NTO.

2 Background

2.1 The light reactor concept

The light reactor concept developed by TNO for the conversion of carbon dioxide and water to ethylene and subsequently to ethylene oxide, see Figure 1, will be adapted to enable the photochemical nitration of compounds using nitrogen dioxide as the nitrating agent. The first step will be the optimization of the photochemical process using a well-known precursor, i.e. benzene, allowing the validation of the reactor system based on literature data. The advantage of nitrogen dioxide over nitric acid is that no water is formed during the reaction that may interfere with the reaction and/or subsequent post processing steps (e.g. purification, recrystallisation).

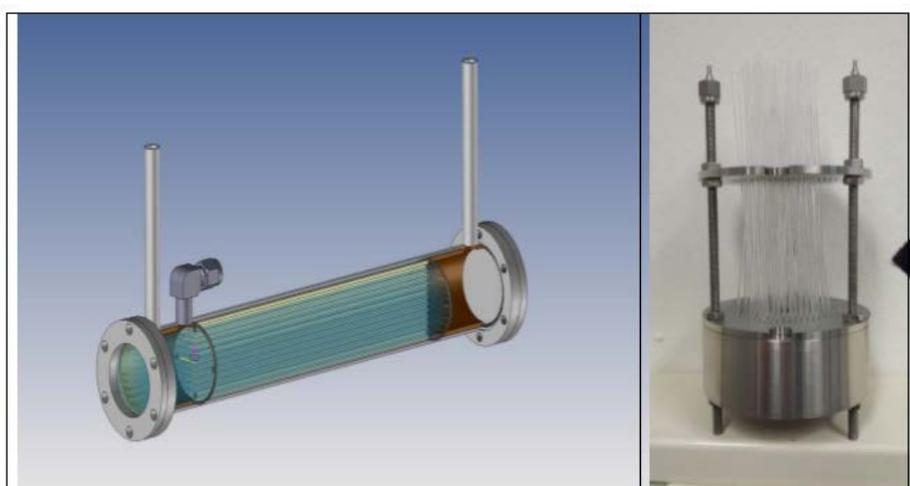


Figure 1. Light reactor developed by TNO for the conversion of carbon dioxide to ethylene. On the left, a schematic of the complete reactor with monolith (made largely transparent for viewing purposes); on the right, the sapphire glass rods with a metal support. It can be used in the reactor without the monolith.

The photocatalytic reactor is based on a flow cell with a monolithic block inside to channel the flow. The reactor can also be used without the monolithic block. Inside the square holes of the monolith, using small rubber rings, sapphire glass rods of 1 mm thickness are placed. The rings do not close the holes entirely and are merely intended to center the rods in their position. In this way it is possible to coat either the rods, the walls of the monolith or both with a catalyst. As can be seen in Figure 1, the rods rest on an optical window (left side of Figure 1). Through the window, light of the desired wavelength can be transmitted into the rods, and with that, the photons are transported into the monolith. This is done by using LEDs with wavelengths that activate the nitrogen dioxide molecule as determined by UV-VIS spectrometry. The advantage of LEDs is that they can have very narrow wavelength band emissions, so that the radiation is more effectively used, compared to a standard lamp (e.g. Halogen lamp) where only a fraction of the emitted light can be used for activation.

Between the optical window and the monolith, glass pearls of the desired particle size can be introduced to distribute the reactant gas flow over the monolith. On the other side of the photocatalytic reactor, the gas is collected and can be sampled using, for instance, a GC-MS. That side of the reactor has a blind that can be replaced with another flange should *in situ* measurements be deemed useful, like FTIR. The reactor is double walled (not shown in Figure

1) to allow for a heat transfer liquid to be circulated. The temperature of the reactor can be varied between -60 and +350 °C. The reactor including windows, can withstand 25 bars of pressure, with the thickness of the windows being the limiting factor. Thicker windows will allow for a higher pressure to be applied.

WP 1: Validation of the light reactor

The light reactor shown in Figure 1 will be validated by photochemically nitrating benzene with nitrogen dioxide. As the activation of the nitrogen dioxide is wavelength dependent and only influences the reactivity of this substance, the optimization of the wavelength will be used in the subsequent work packages.

Specific tasks:

- 1) Adjustment of setup to allow for nitration reactions to be executed (changing O-rings, checking compatibility of valves, et cetera).
- 2) Determination of the optimum wavelength for activating nitrogen dioxide. This is done by UV-VIS spectrometry and checked with available literature.
- 3) Assessment of the flow speed needed to ensure nearly complete depletion of nitrogen dioxide at the exit of the flow reactor (residence time).
- 4) Determination of yield and selectivity as a function of wavelength.
- 5) At optimum wavelength, variation of temperature of the reactor to assess its influence on yield and selectivity. Preferably, the closer the temperature to room temperature, the lower the utility costs (heating, cooling).
- 6) Assess the effect of the addition of oxygen on the yield, selectivity and reaction rate.

2.2 Determination of optimum wavelength

From literature, it is known that NO₂ absorbs in the both ranges (UV and VIS) over a wide range. It is also known from literature [3] that at wavelengths of 365 and 436 nm, nitrogen dioxide can be activated to become chemically reactive. What needs to be ensured is that benzene will not be unfavorably activated in this range leading to unwanted byproducts and that the produced mono-nitrobenzene should not decompose. By checking the fingerprint of these substances with the UV-VIS spectrometer as well as mixtures of these substances, the most appropriate wavelength can be chosen for the light reactor.

It should be noted that the mixture of nitrogen dioxide and oxygen [3], upon careful selection of the wavelength, can also lead to the formation of the powerful gaseous nitration mixture of NO₂ plus ozone [1, 3]. Although relatively easy to achieve and keeping in mind that this concept needs to be integrated into a large-scale production system, the concentration of ozone in the outlet stream of the reactor and effects of ozone on the post-processing systems need to be considered. As such, the production of ozone is a welcome in terms of nitration, but it may negatively affect post-processing processes.

Benzene and nitrobenzene both absorb in the visible light range as known from literature. See for literature spectra of these substances the next paragraph.

In order to activate nitrogen dioxide with a dedicated wavelength and avoiding the activation of other molecules present in the system (oxygen, benzene) leading to unwanted side-products with the same wavelength, a UV-VIS spectrometer can be used. A second reason to use a UV-VIS spectrometer is that the conversion can be followed due to the appearance and

disappearance of peaks in the spectrum. By making calibration curves as a function of concentration, the absolute consumption or production of a species can be determined.

With the UV-VIS spectrometer, the absorbance of light by a substance as a function of wavelength can be scanned in a matter of minutes. It should be noted that when using gaseous species (like NO₂), the concentration also becomes a relevant parameter as this should be above the detection limit of the spectrometer.

From oxygen, it is known that it will not absorb in the visible range, but will do so in the deep UV range, yielding ozone among other species. From a practical point of view, the use of UV light with the light reactor is not recommended for a number of reasons.

- 1) UV light is hazardous to personnel when exposed to a high intensity of light. It tends to be well absorbed by numerous media (including oxygen from air), hereby decreasing the amount of energy effectively used for the chemical conversion of nitrated species.
- 2) The incorporation of UV light with a large-scale reactor is cumbersome, as specific precautions are needed, making the system complex.

2.3 Spectra

The relevant spectra available in literature are presented below, of the species present during the conversion of benzene to mono-nitrobenzene.

2.3.1 Oxygen

O₂ does not absorb in the VIS region but does so just in the UV-region.

Figure 2. Deep-UV absorption spectrum of oxygen [16].

2.3.2 Nitrogen dioxide (NO₂)

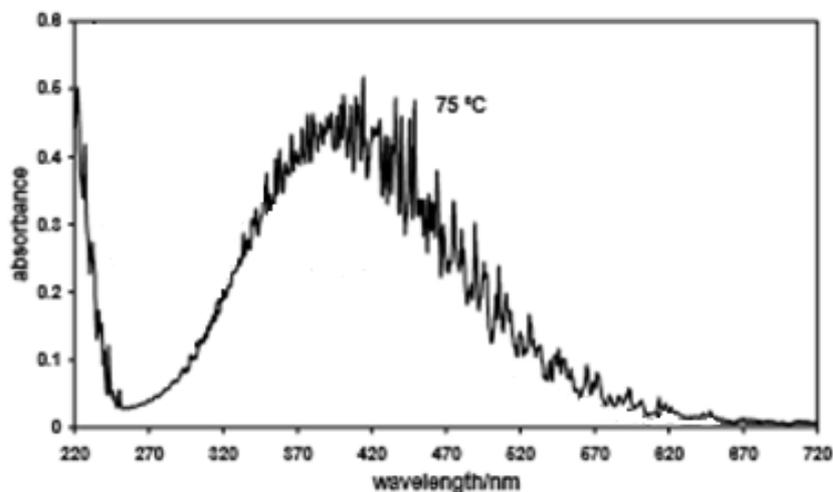
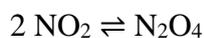


Figure 3. Absorption spectrum of NO₂ measured at 75 °C [17].

As a first step in proving the viability of solventless, photochemical nitration, the gas phase nitration of benzene is selected. This means that the temperature applied in the reactor needs to be such that benzene is in the gas phase (i.e., at a temperature above the boiling point of benzene). A lower temperature is possible, but this means that benzene will be in both the liquid and gas phase and that the nitration reaction will occur in the gas phase as well as at the interface of the liquid benzene with the gas phase above it. Furthermore, at elevated temperatures the formation of dinitrogen tetroxide (N₂O₄) is avoided. Nitrogen dioxide (NO₂) is a reddish-brown gas above 21.2 °C, a yellowish-brown liquid below 21.2 °C, and it converts to colorless pure N₂O₄ below -11.2 °C. As such the equilibrium reaction of NO₂ to N₂O₄ is presented as follows:



The higher the temperature, the more this equilibrium shifts to the left. Dinitrogen tetroxide absorbs light in the deeper UV range, compared with nitrogen dioxide.

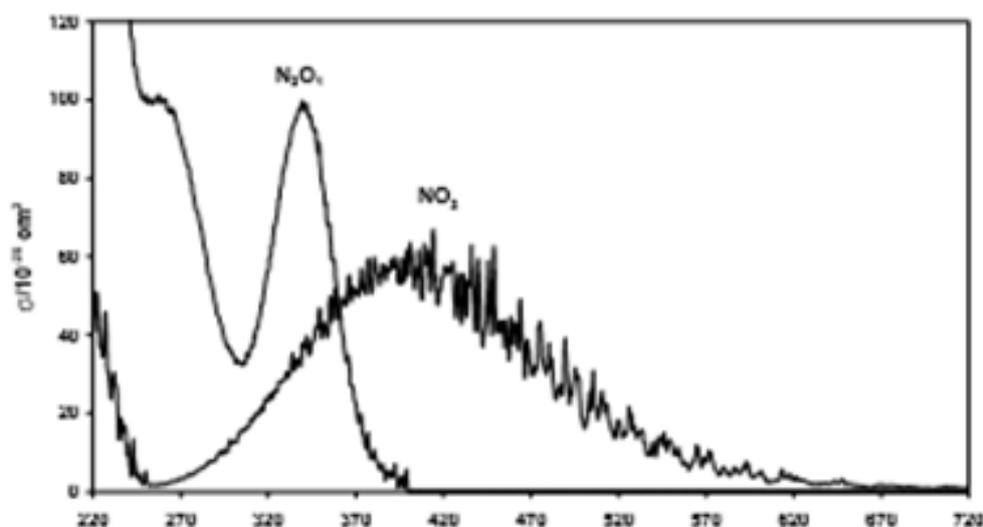


Figure 4. Absorption spectrum of NO₂ and N₂O₄ measured at 5 °C and 75 °C [17].

2.3.3 Benzene

Benzene does not absorb light beyond 300 nm. The spectrum of benzene is given in Figure 5 [18].

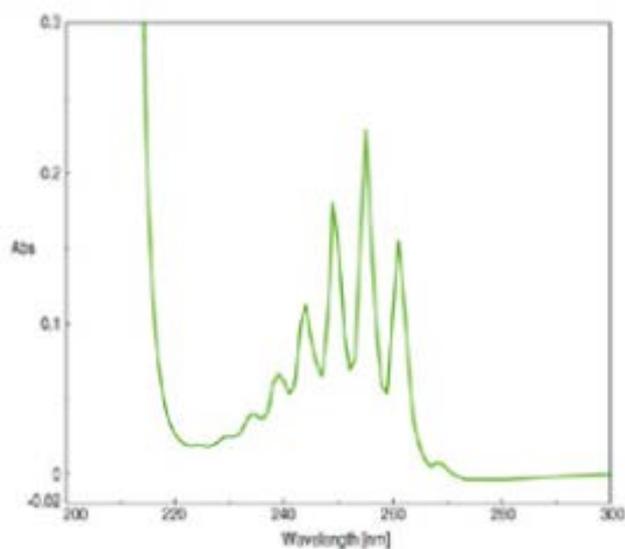


Figure 5. Absorption spectrum of benzene [18].

The spectrum of benzene as given in Figure 5 is a detailed one with peaks at a defined range with a very slow scan. As molecules have various excited modes (vibration and rotation), absorption is usually over a wide range of wavelengths. These transitions are spaced too closely to each other that a standard UV-VIS spectrometer on standard settings will not be able to resolve them. The spectrometer instead will trace an envelope of the pattern.

2.3.4 Nitrobenzene

The spectrum of nitrobenzene is largely similar to that of benzene, with the exception of the presence of a shoulder near 220 nm, see Figure 6 [19].

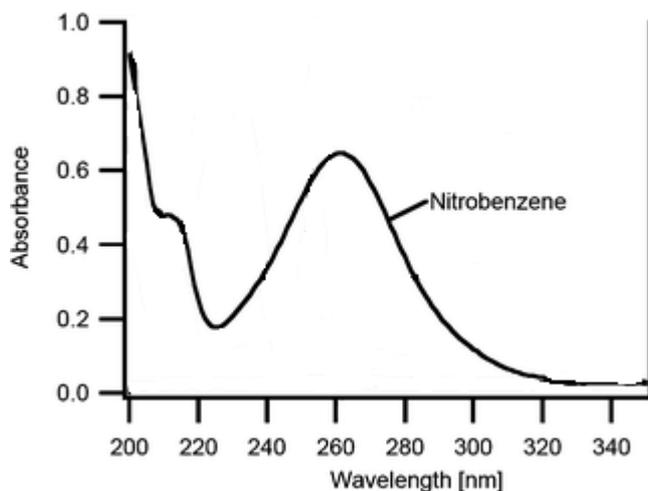


Figure 6. Absorption spectrum of nitrobenzene [19].

As mentioned in the previous section, a standard UV-VIS spectrometer will not be able to resolve all excited modes of the molecules and as such, measure this as one peak, as can be clearly seen in Figure 6. To resolve the excited modes a more advanced spectrometer is needed.

2.4 Conclusions

From the literature data concerning the UV-VIS absorbance of the different pure substances, it can be concluded that the optimum wavelength needed for activation of nitrogen dioxide does not interfere with an absorption band of any of the other substances that are present during the experiments. The only open question is that there might be potential second order effects when a mixture is present in the reactor that may cause interference, although considered unlikely due to the nature of the molecules.

3 Experimental Setup

3.1 Introduction

In this chapter the experimental equipment used is detailed, supplemented with the experimental methodology when needed. In Section 3.2 the work plan will be presented to perform solventless nitrations by the photochemical activation of nitrogen dioxide. In Section 3.3 the UV-VIS spectrometer is detailed and in Section 3.4 all batch operated test vessels are described. The fluidized bed reactor is detailed in Section 3.5 and in Section 3.6 the microwave reactor is presented.

3.2 Work plan

A wide range of NO₂/benzene ratios, temperatures, and catalyzing agents have been reported for the gas-phase nitration of benzene [2, 3]. However, no systematic studies on the influence of these parameters on each other and on the yield are known. To systematically investigate the influence of these parameters, with a goal of as short reaction/residence time as possible, combined with the highest possible yield, the following experimental setups or equipment were selected:

- 1) Using a UV-VIS spectrometer to determine at the selected wavelength(s) for the activation of the nitrogen dioxide, that there would be no interference with the other compounds present in the systems, eliminating unwanted by-products.
- 2) A lab scale batch reactor system to be used to systematically assess the ratio NO₂/benzene, temperature, and reaction time required for conversion of benzene to nitrobenzene.
- 3) A continuous flow system. The knowledge obtained with the lab scale batch reactors is used as a starting point for selecting conditions for operation of a continuous flow system, here referred to as the light reactor. The light reactor is to be prepared for receiving pure nitrogen dioxide under the given operating conditions, without compromising any of the components present.

3.3 UV-VIS Spectrometer

The spectra were recorded using a Shimadzu UV-mini-1240 spectrometer and the results were analyzed using the UV Data Manager 1.03 software package. A quartz, double walled cuvette was purchased from Hanna Analytics. The cuvette allows for the circulation of a heating/cooling liquid and had a light path of 10 mm (article number 160-001-10-40). Measurements were done at atmospheric pressure and both at room temperature and at 90 °C to allow for gaseous benzene and NO₂ to be measured. The spectrometer used had a spectral range of 190-1200 nm. Measurements were scanned in the range of 200-1000 nm, covering the wavelength ranges presented in Chapter 2, as the wavelengths of interest are in the visible range. Gas measurements were done with the cuvette stoppered.

3.4 Lab scale batch reactor setups

3.4.1 *Setups used for task 1*

In Figure 7, the adapted TNO light reactor is shown. In this work package, no experiments were planned with this reactor, but the system was tested for compatibility at the given conditions, especially in terms of the higher temperatures employed in combination with the gaseous nitrogen dioxide.

The light reactor was built to withstand pressures up to 50 bar and temperatures up to 325 °C. Although not directly necessary for this project, it allows for a wide range of application possibilities. In order to withstand the temperatures, the sealants were of the Kalrez type. For lower temperatures, Viton sealants were used.

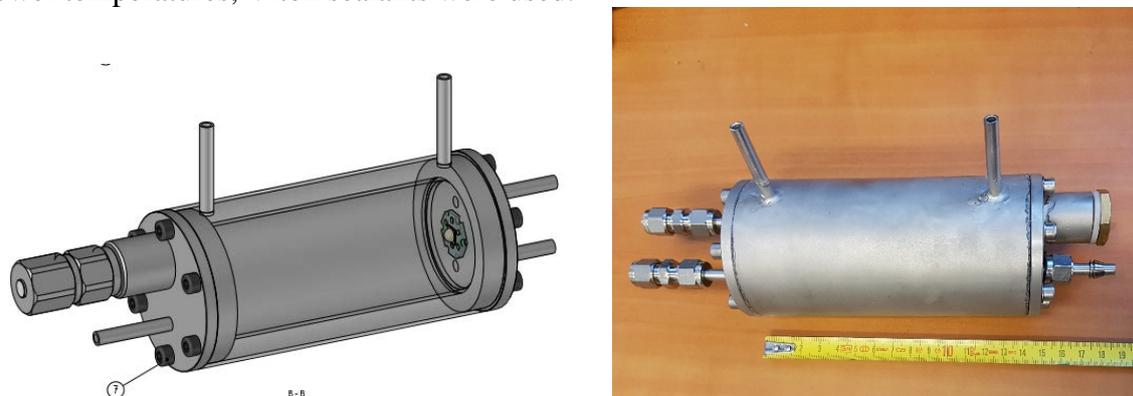


Figure 7. Light reactor schematic (left) and photo (right).

Molar ratios NO_2 :benzene varying from 80:1 down to 0.007:1 have been reported in literature for the nitration of benzene by NO_2 . The highest yields (10 - 80%) were obtained using excess NO_2 . Addition of 30-80% O_2 significantly increased the reaction rate and yield [2].

Based on technical feasibility and expected yields, NO_2 :benzene ratios between 25:1 and 1:1 were explored first, without addition of oxygen. Initially, the reaction temperature was chosen ≥ 90 °C, above the boiling point of benzene, to ensure all reactants were in the gas phase. For continuous flow reactions, short residence times are preferred, whereas typical literature reaction times vary from 1.5 up to 456 hours at room temperature [3]. A wide range of reaction times were evaluated varying from hours to minutes, in order to evaluate the minimum reaction time required to obtain significant yields and selectivity and with that the required residence time in the light reactor.

After determination of a suitable wavelength for excitation of NO_2 based on the UV-VIS measurements, a setup was developed for the gas-phase nitration of benzene. The initial layout of the setup is shown in Figure 8. A three-necked round bottom glass flask was evacuated while being heated to the reaction temperature in an oil bath. After closing the line to the vacuum pump, benzene was added via a septum and subsequently the flask was filled with NO_2 up to 1 bara via stainless steel and Teflon tubing. The pressure in the system was evaluated using a pressure indicator (0 – 2.5 bara) located in the stainless steel NO_2 line. A LED (output 0.8 W, $\lambda = 355 - 375$ nm) hanging in the flask was used to facilitate photo-initiation of the nitration reaction. Optionally O_2 could be dosed to the flask prior to NO_2 introduction to catalyze the reaction. After the reaction, the product was cooled to 0 °C, dissolved in deuterated chloroform and analyzed using NMR. After degradation of the LED by NO_2 and its subsequent break-down, the setup was slightly modified, and a glass window was used to separate the LED from the gaseous phase inside the reactor.

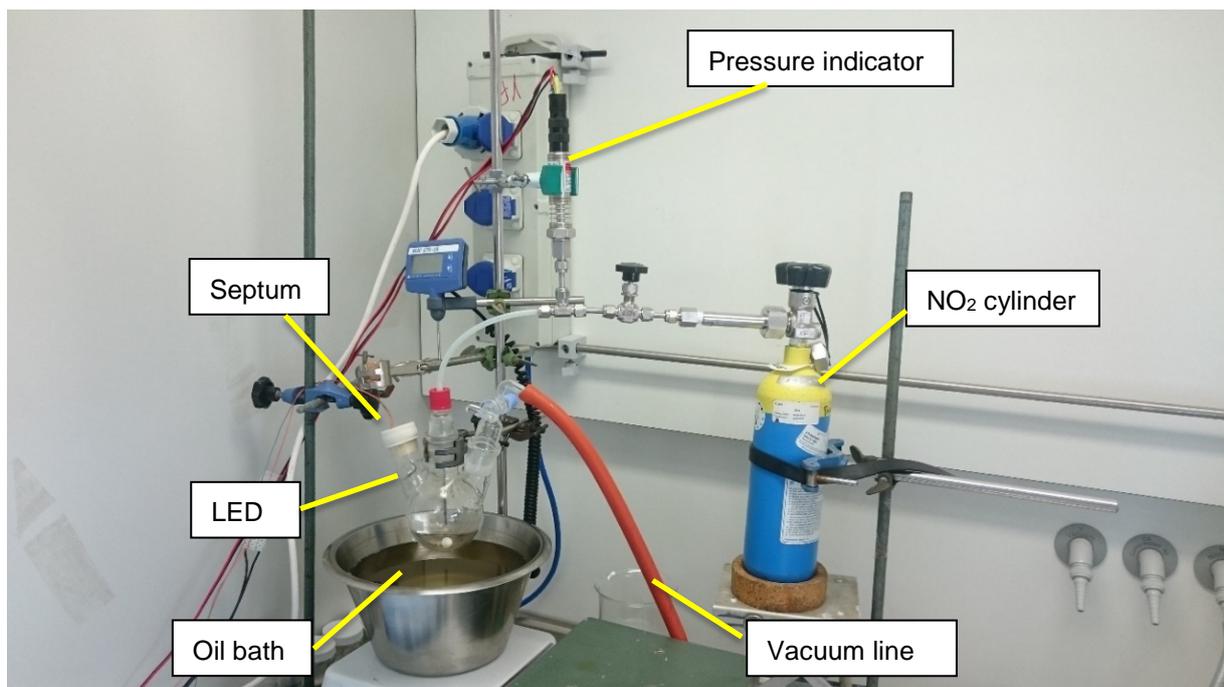


Figure 8. Experimental batch test setup for initial nitration tests and material compatibility evaluation.

After initial experiments using this versatile setup, a robust stainless-steel reactor was built for systematically evaluating the influence of reaction conditions on the product yield, without having to consider the fragility of the glass-based system.

The major difference with the glass reactor is that the stainless-steel reactor was heated by a heating plate instead of with an oil bath. It furthermore was insulated to reduce the heat loss. For the stainless-steel reactor, the experimental methodology was identical to that used with the glass reactor as described above.

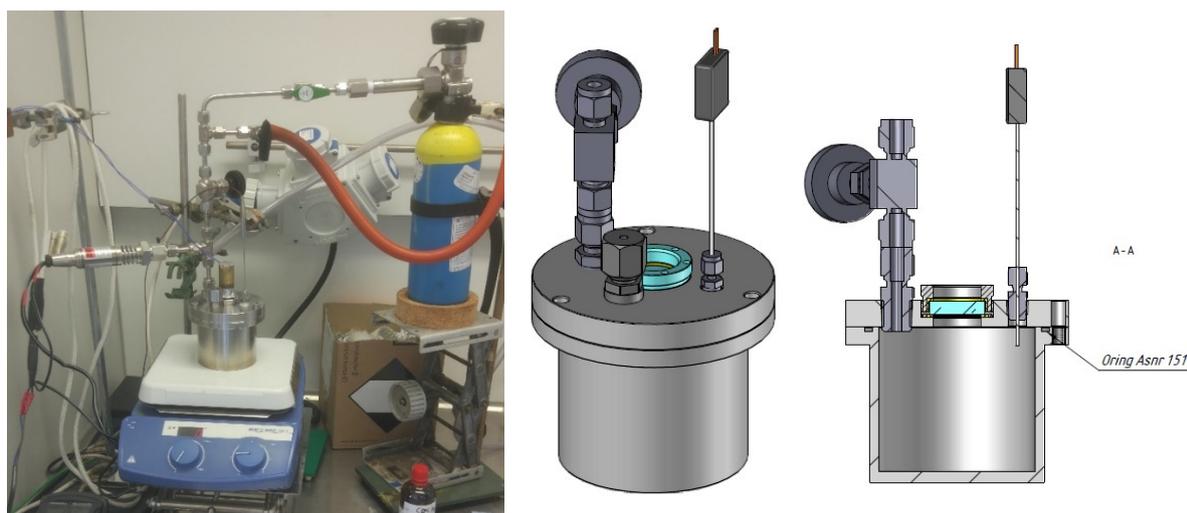


Figure 9. Stainless steel batch test setup for investigating the optimum NO₂:benzene ratio, temperature and residence time. On the left the setup as used with the insulation removed for clarity and on the right schematics of the vessel. In the drawings on the right the light source is not present and only the optical access (window) is shown. In the photo on the left the LED is the copper colored structure in the center of the vessel.

3.4.2 Setups used for task 2

Besides oxygen and light, a range of catalysts was reported to catalyze the nitration of organic molecules, including metal oxide and zeolite catalysts like Na-ZSM-5 [4], WO_3/ZrO_2 [9] and ZSM-5 [12].

For the batch reactor tests the solid catalysts were deposited on the bottom of the reactor, as the goal of the experiments was to see if the catalysts would have a positive effect on the reaction time. The interaction between the catalysts and the reaction medium (highest possible specific surface area) was not optimized. To enhance the interaction between the gaseous reaction medium and the catalyst, glass rods were applied to transfer light to the bottom of the reactor. The introduction of the glass rods was also performed in anticipation of the fluidized bed experiments to be executed with tasks 3 and 4. A bundle of seven glass rods, each having a core diameter of 15 mm, and a highly chemical resistant Tefzel coating was prepared and fitted in one of the necks of the glass reactor, see Figure 10.

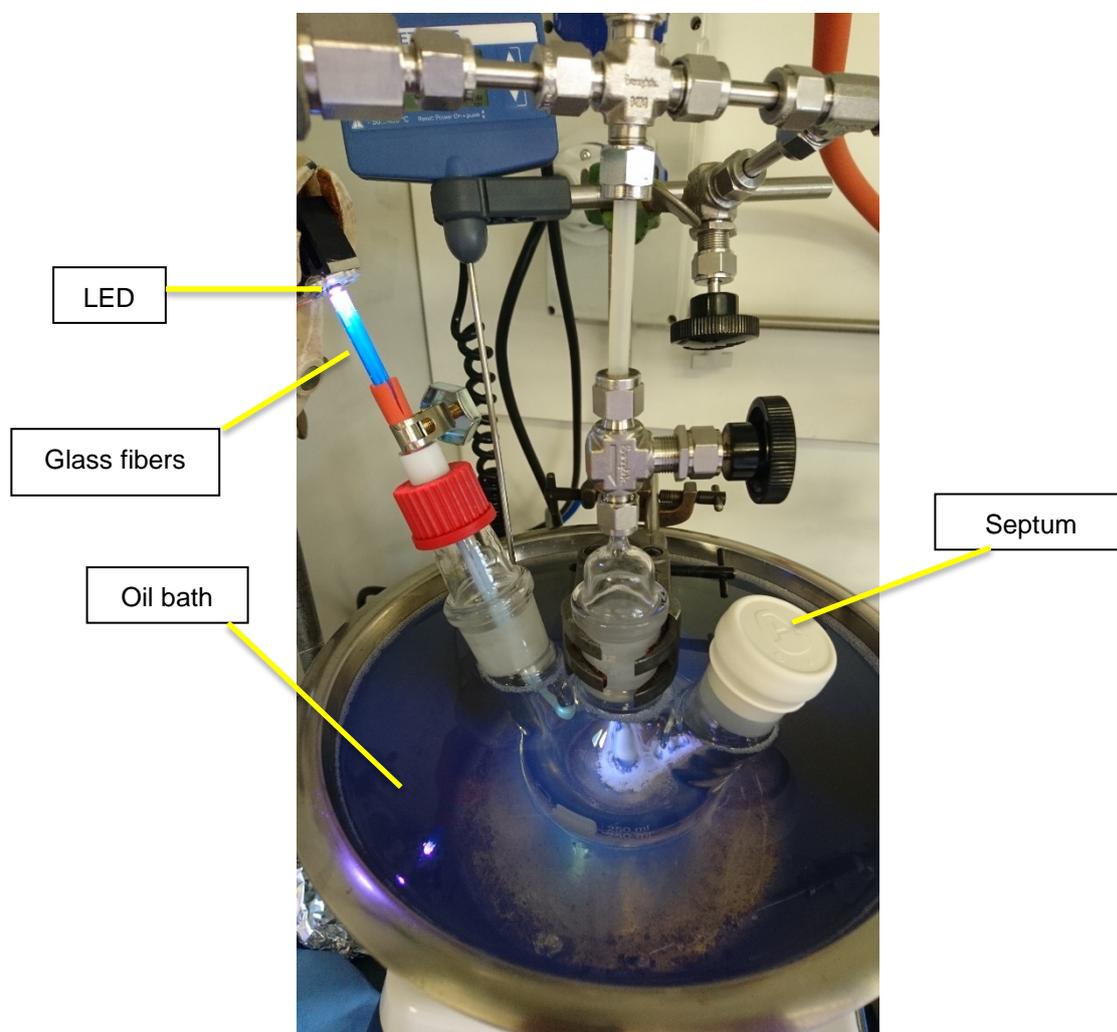


Figure 10. Part of the reactor setup for evaluating the influence of solid catalysts on the product yield. Light was introduced via a bundle of glass rods.

First, 0.25 g of the solid catalysts was placed at the bottom of the flask. The tested catalysts were a metal catalyst (chromium powder), a zeolite catalyst (NH₄-ZSM-5), an acid zeolite catalyst (H-ZSM-5) and an acid metal oxide catalyst (niobic acid). After catalyst introduction, the flask was brought to the reaction temperature, evacuated and stirred using a Teflon coated magnetic stir bar. Oxygen, benzene and NO₂ were dosed (total gas pressure ~ 0.9 bara) and the LED was illuminated. After the desired reaction time, the LED was switched off, the flask was allowed to cool to room temperature and subsequently cooled in ice for ~ 30 minutes. 3 mL of deuterated chloroform was added to the flask, aiming to quantitatively dissolve all reactants and products. After settling of the solid catalyst particles, the supernatant was, after addition of an internal standard (nitromethane), analyzed using ¹H NMR.

The stainless-steel reactor was used for systematically testing catalysts according to the methodology protocol described in section 3.3.1. Compared to the glass reactor (better sealing), the stainless steel reactor gave more accurate results. The reactor was used unmodified, i.e., the LED was mounted on top of the reactor and no fibers were introduced. In this vessel 1 gram of the powdered catalyst was distributed on the bottom of the vessel. The catalysts used were the same as with the glass reactor and additionally zirconium oxide, tungsten oxide, the zeolite catalyst NH₄-ZSM-5, aluminum silicate and Nafion were tested.

3.5 Fluidized bed reactor setup

For the reaction between a gas and a solid, a fluidized bed reactor system was selected. A glass reactor was designed and built in which 1,2,4-triazole-5-one, the solid reactant for the solventless nitration to NTO, could be fluidized in an NO₂-flow while being heated or cooled and illuminated inside the fluidized reactor bed, see Figure 11. For the fluidized bed the bundle of glass rods developed for the glass batch reactor was used to facilitate the illumination inside the bed.

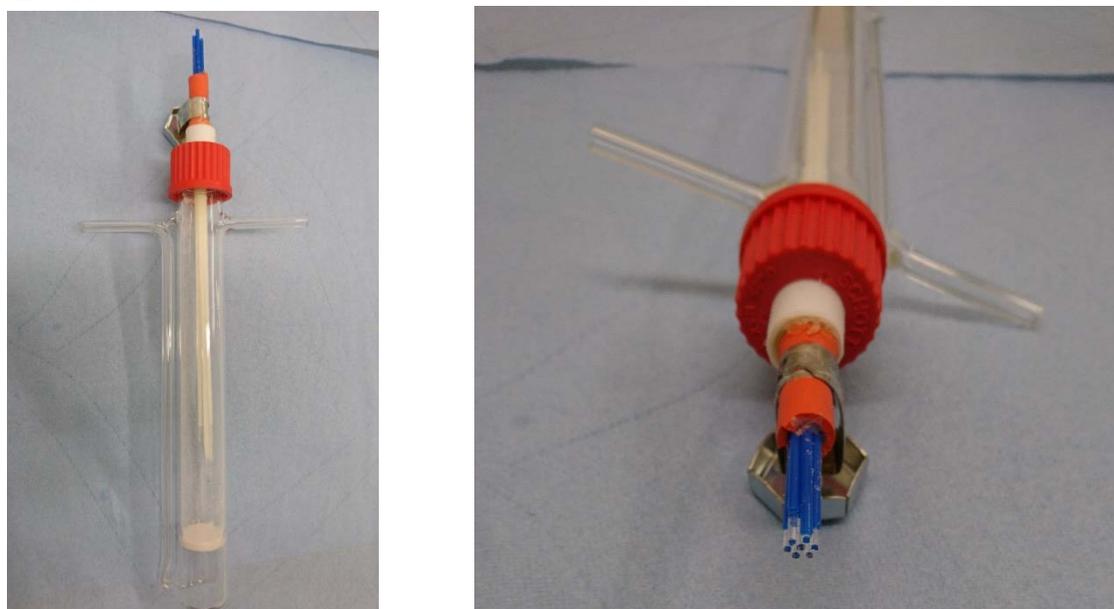


Figure 11. Fluidized bed reactor for the solventless nitration of TO to NTO. On the left the fluidized bed and on the right a close-up of the bundle of glass rods.

The bottom of the reactor up to the mount holding the bundle of glass rods can be placed in a bath for heating or cooling purposes. Through the top end of the reactor, the bundle of seven glass rods was mounted, transferring light from an LED into the fluidized bed. Another benefit

of the application of a glass reactor is that without further modification a microwave source, potentially required for catalyzing the reaction, can be applied (task 4).

1 gram of a 63-125 μm fraction of 1,2,4-triazole-5-one was placed on the glass filter in the reactor. Using a Brooks GT1355 Sho-Rate G flowmeter, a 1 L min^{-1} flow of 10 vol% NO_2 in N_2 is led to the bottom of the reactor and fed through the reactant bed.

3.6 Microwave reactor

The fluidized bed was designed in such a way that microwave elements could be placed around it to assess if microwave radiation would help in reducing the reaction time. As this would imply that specific elements needed to be bought but more importantly, that the safety of the people working with the new setup needed to be guaranteed, it was decided to first make use of a commercially available microwave reactor present at TNO. In this setup the LED system cannot be introduced. If microwave radiation has an effect on the conversion of the nitration reaction, the combination of both LED and microwave radiation is, however, not likely to intervene with each other.

The commercial microwave reactor available at TNO is shown in Figure 12.



Figure 12. Commercial microwave reactor Biotage Initiator Plus used for the assessment of the effectiveness of microwave radiation on the nitration reaction.

In the Biotage Initiator Plus microwave system disposable borosilicate vials of different volumes can be placed. In total 64 vials can be prepared and the system will irradiate these vials sequentially. For the nitration reactions the largest possible vials were used (31 mL). The system was programmed to have the vials irradiated for 10 minutes with microwave irradiation. Prior to that, the microwave was allowed to heat up to $40 \text{ }^\circ\text{C}$, the minimum operating temperature of the system. To assess the effectiveness of the microwave radiation, nitration reactions were performed in the gas phase (nitration of benzene to nitrobenzene) and with the solid – gas phase system of TO to NTO. It should be noted that the latter mixtures obviously could not be fluidized, as a dedicated system was used. However, during all tests the mixtures were well stirred to at least make sure the nitrogen dioxide could come in contact with the TO powder.

4 Results & Discussion

4.1 Introduction

In Section 4.2 the experimental solventless photochemical nitration of benzene is described. Because of the importance of UV-VIS to monitor the progress of nitration, first blanks are measured of reactants, products and carefully controlled mixtures. In Section 4.3 the effect of the addition of catalyst on the photochemical nitration of benzene is given. The photochemical nitration of 1,2,4-triazole-5-one to nitro-1,2,4-triazole-5-one is given in Section 4.4. In Section 4.5 the microwave assisted nitration of both benzene and 1,2,4-triazole-5-one is reported.

4.2 Task 1: Solventless photochemical nitration of benzene

4.2.1 UV-VIS spectra

The chemicals used for the UV-VIS measurements were used as received. The nitrobenzene (99%) and benzene (99%) were purchased from Sigma Aldrich, whereas the nitrogen dioxide and oxygen were purchased from Air Liquide.

Before every UV-VIS measurement, a blank measurement was taken so that measured spectrum can be compared with this blank to ensure that peaks from sampled spectra indeed belong to the sample and are not due to absorptions of the cuvette, ambience stray light or air. For the blank measurement, nitrogen was used as reference gas.

When the gases nitrogen dioxide and oxygen were measured, the cuvette was flushed with these gases to ensure no air was present. Benzene and nitrobenzene were placed in the cuvette in liquid form and while heating, the vapor pressure of these two compounds expelled the air from the cuvette.

4.2.1.1 Oxygen

As oxygen does not absorb in the scanned UV-VIS range as employed here, the recorded UV-VIS spectrum in Figure 13 is identical to that of the blank (not shown).

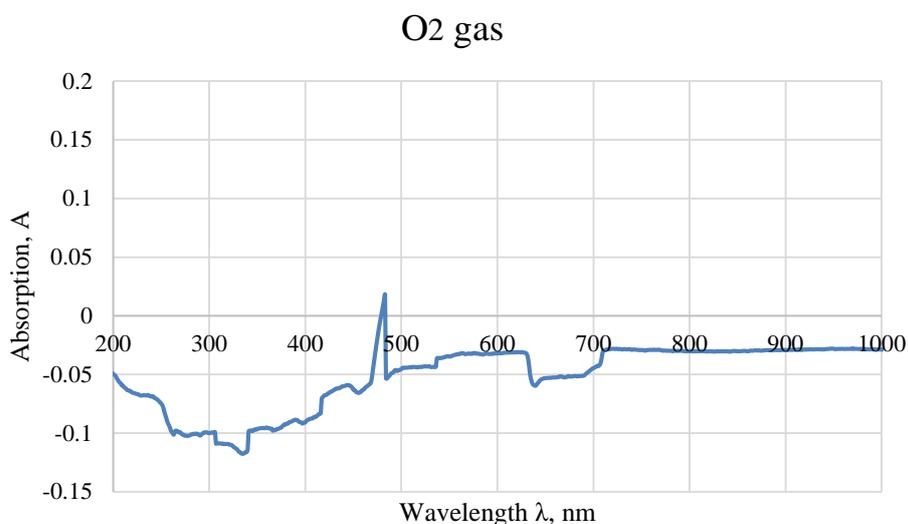


Figure 13. UV-VIS spectrum of oxygen.

4.2.1.2 Nitrogen dioxide

The UV-VIS spectrum of nitrogen dioxide was recorded at room temperature, see Figure 14. As can be seen, it resembles the NO₂ reference spectrum from literature (Figure 4). This means that it is present in the NO₂ form instead of the N₂O₄ form at room temperature.

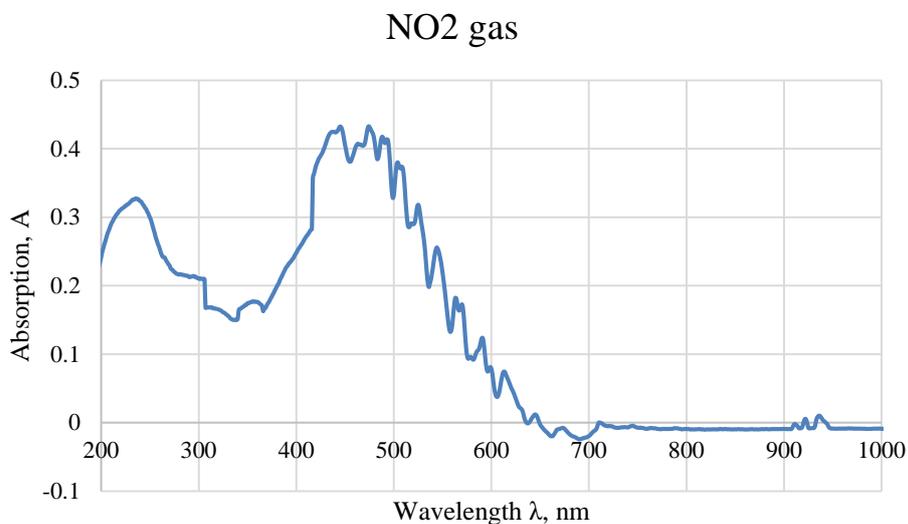


Figure 14. UV-VIS spectrum of nitrogen dioxide.

4.2.1.3 Benzene

The recorded UV-VIS spectrum of benzene is shown in Figure 15. For this project, it is more important to know where the absorption bands are located and as such the scanning rate was too high to resolve the excited modes visible in Figure 5.

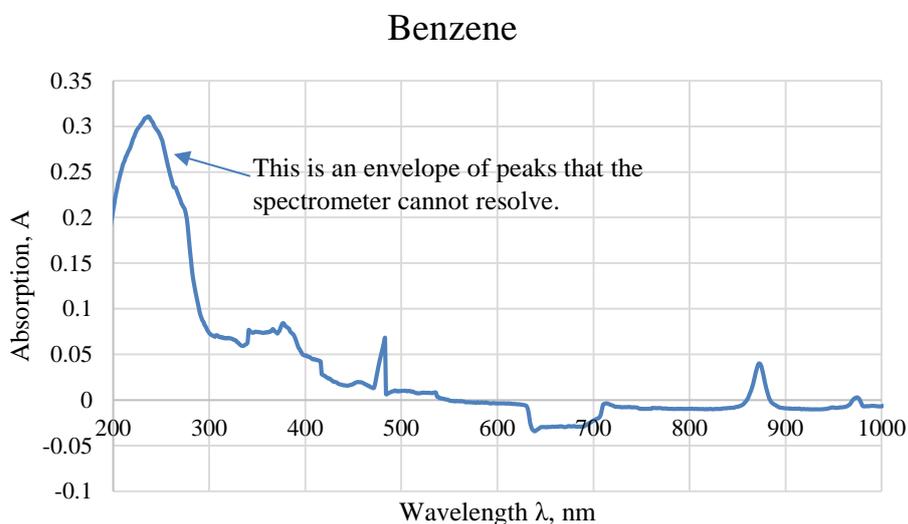


Figure 15. UV-VIS spectrum of benzene.

4.2.1.4 Nitrobenzene

The recorded UV-VIS spectrum of nitrobenzene is presented in Figure 16.

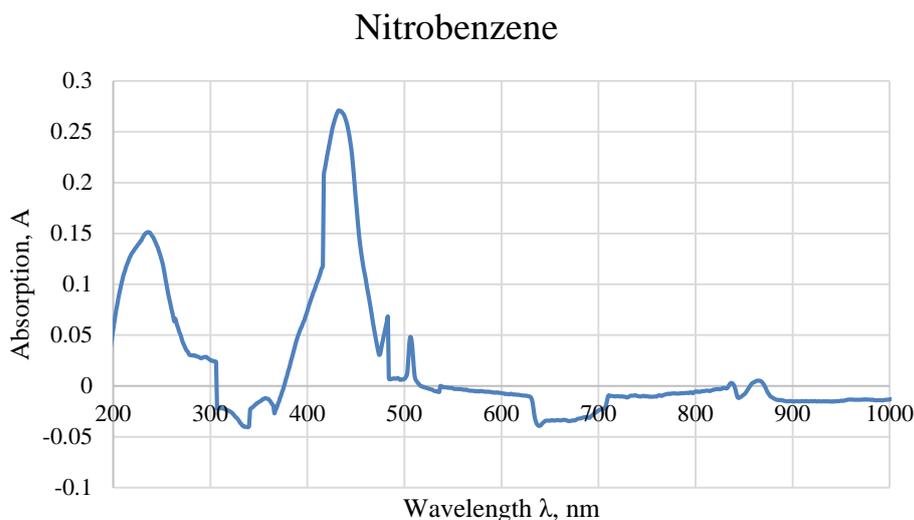


Figure 16. UV-VIS spectrum of nitrobenzene.

Comparing the reference spectrum as given in Section 4.3.4 (Figure 6), a peak appears in the range between 400 and 500 nm in the measured spectrum. This peak is related to the color of the commercial sample of nitrobenzene supplied, which was slightly yellow. Nitrobenzene is often either transparent or clear yellow, dependent on the producer. A yellow colored liquid has to produce a peak or peaks between 435 – 480 nm.

4.2.1.5 Mixtures

In Figure 17, the recorded UV-VIS spectrum of a 50:50 wt% mixture of benzene and nitrobenzene is shown. As can be seen, the spectrum is a superposition of the benzene and nitrobenzene curves and hence no higher order effects are present.

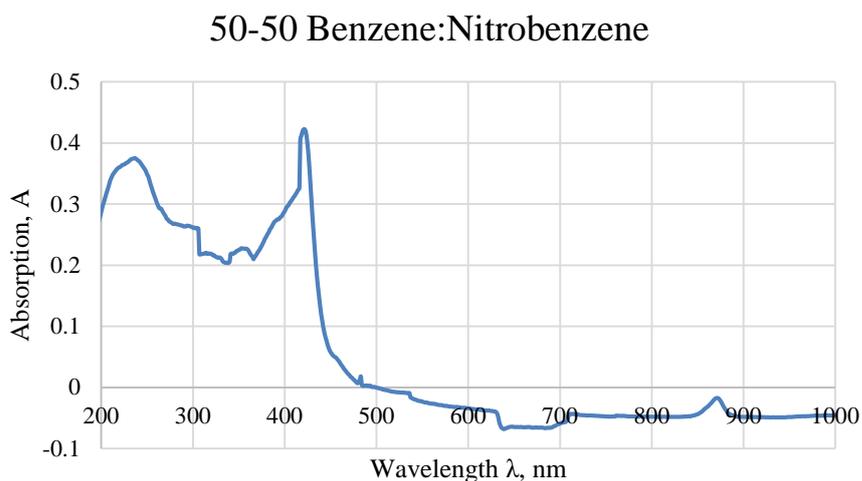


Figure 17. UV-VIS spectrum of a 50:50 benzene:nitrobenzene mixture.

Mixtures of benzene with oxygen and nitrobenzene with oxygen were deemed unnecessary due to the fact that oxygen does not absorb in the wavelength range studied.

4.2.1.6 Conclusions.

Based on the UV-VIS experiments, it is concluded that the relevant reactants and products are not expected to generate any higher order interactions that may lead to unwanted byproducts or the decomposition of nitrobenzene itself. For the activation of the NO₂ molecules for nitration purposes, a wavelength around 365 nm will be used. In order to have narrow wavelength band, a LED will be used for this purpose.

4.2.2 Lab scale batch experiments

Initial experiments were performed to study the feasibility of gas phase nitration of benzene by NO₂. For these reactions a glass flask with an LED was applied as described in Figure 8.

In one experiment with the batch reactor setup the LED was hanging in the flask, 60 μ L (0.67 mmol) liquid benzene and 210 mL NO₂ (6.9 mmol) were illuminated for 2 hours at 90 °C. After cooling the flask to 0 °C, 20 mL hexane was injected into the flask to dissolve the product and potential remaining reactants. Based on GC-MS analysis, both nitrobenzene (66 μ g/mL) and benzene (422 μ g/mL) were found to be present in the mixture. The low yield of nitrobenzene (11 μ mol, 1.6 mole%) indicates that only a small amount of benzene was converted.

As the coupling of the LED into the lab scale batch reactor is far from straightforward, several options were tested. With the first experiments, the LED was placed inside the round bottom flask. As the maximum temperature the LED can withstand is 80 °C, while the flask itself was operating at 90 °C, the LED stopped working after 30 minutes. Also, the distribution of the light inside the reactor was far from optimal. In the next experiments, the LED was placed outside the flask on top of the septum to allow the light to reach the inside of the flask. Under these circumstances the LED also could not handle the temperatures it was exposed to. Furthermore, the protective dome around the diode was directly attacked by the nitrogen dioxide, herewith destroying the diode. Due to degradation of the LED by NO₂ and subsequent failure, only a limited number of experiments were performed using this configuration. It should be noted that the gradual breakdown of the light source during the experiment, the light intensity may have decreased in time, lowering the yield.

In the next experiments, the LED transmitted the light via a glass window, the diameter of which was equivalent of the septum or connected with a glass rod which was allowed to pierce through the standard septum. In both cases, the LED was capable of dissipating sufficient heat to properly operate, but the quantum efficiency dropped significantly due to far less photons being capable of interacting with the nitrogen dioxide.

In Table 1 the results obtained with the batch reactor are detailed. In experiment 1, the LED was emitting through a 4 cm glass rod. In experiments 2 to 4, the LED was placed on top of a 1 mm thick glass window. Although the irradiation was not ideal (low quantum efficiency) and the exposure time limited, the yield was acceptable.

Table 1. Initial results obtained with the glass batch reactor.

| Experiment # | Time [min] | Temperature [°C] | NO ₂ /benzene molar ratio [-] | O ₂ /benzene molar ratio [-] | Yield [mole%] |
|--------------|------------|------------------|--|---|---------------|
| 1-1 | 30 | 90 | 10 | 0 | < 1 |
| 1-2 | 30 | 90 | 9 | 0 | 9 |
| 1-3 | 30 | 90 | 9 | 0 | 13 |
| 1-4 | 30 | 90 | 7 | 3 | 11 |

Table 2. Results of the solventless photonitration of benzene with nitrogen dioxide as a function of NO₂:benzene:O₂ molar ratio, temperature and reaction time. Results are averaged over at least 2 measurements. Tests were performed at an initial pressure of 1 atmosphere absolute, unless indicated otherwise. Please note that the reference measurements are performed without the light source (vessel was sealed to prevent any ambient light from entering).

| NO ₂ :Benzene:O ₂ molar ratio [-] | Temperature [°C] | Reaction time [h] | Yield Nitrobenzene [mole%] | Remark |
|---|---------------------|----------------------|----------------------------------|---------------------|
| 10:1:0 (reference) | 100 | 2.5 | < 1 | No LED illumination |
| 3:1:0 | 100 | 2.5 | < 1 | |
| 10:1:0 | 100 | 2.5 | < 1 | |
| 25:1:0 | 100 | 2.5 | < 1 | |
| | | | | |
| 3:1:0 | 100 | 7.0 | 1 | |
| 10:1:0 | 100 | 7.0 | 2 | |
| 25:1:0 | 100 | 7.0 | 2 | |
| | | | | |
| 10:1:0 | 100 | 2.0 | 4 | 1.75 bara |
| 10:1:0 | 100 | 2.0 | 3 | 1.30 bara |
| | | | | |
| 10:1:0 (reference) | 20 | 4.0 | 3 | No LED illumination |
| 1:1:0 | 20 | 4.0 | 2 | |
| 3:1:0 | 20 | 4.0 | 6 | |
| 10:1:0 | 20 | 4.0 | 17 | |
| 10:1:0 | 20 | 64 | 32 | |
| 25:1:0 | 20 | 4.0 | 40 | |
| | | | | |
| 10:1:16 (reference) | 20 | 2.0 | 28 | No LED illumination |
| 10:1:2 | 20 | 2.0 | 34 | |
| 10:1:8 | 20 | 2.0 | 89 | |
| 10:1:16 | 20 | 2.0 | 96 | |
| 10:2:8 | 20 | 2.0 | 42 | |
| 10:5:8 | 20 | 2.0 | 19 | |
| | | | | |
| 10:1:16 (reference) | 0 | 2.0 | 91 | No LED illumination |
| 10:1:16 | 0 | 2.0 | 93 | |
| | | | | |
| 10:1:16 (reference) | 60 | 2.0 | 8 | No LED illumination |
| 10:1:16 | 60 | 2.0 | 10 | |
| | | | | |
| 10:1:16 | 20 | 0.5 | 33 | |
| 10:1:16 | 20 | 1.0 | 58 | |
| 10:1:16 | 20 | 1.5 | 77 | |
| 10:1:16 | 20 | 2.0 | 96 | |
| | | | | |
| 10:1:16 | 20 | 2.0 | 68 | Air was used |

With the lessons learned from the first few experiments, the batch operated stainless steel vessel was constructed as shown in Figure 9. Considering the reaction times needed (see Table 1) it was deemed more useful to perform experiments with a batch reactor than with the light reactor shown in Figure 7. In order to have meaningful results, a light reactor of several tens up to hundreds of meters would have been necessary to achieve the residence time required. This was considered not useful, unless ways to increase the reaction rate (and hence reduce the residence time) were found in the rest of the project (tasks 2 to 4). To proceed, the light reactor was put aside until more realistic residence times were found. With the newly constructed stainless-steel reactor operated in batch mode, optimum reaction conditions were determined as function of reactant ratio, temperature, pressure and residence time. The results are summarized in Table 2.

4.2.3 Discussion and conclusions

- 1) A high reaction temperature has a negative effect on the yield. At lower temperatures, the yield increases significantly to nearly 100% within the experimental reaction time.
- 2) The more nitrogen dioxide present in the gas phase, the higher the yield.
- 3) At lower temperatures, the yield increases significantly. The amount of benzene present in the vapor phase is limited by the partial pressure of benzene at the given temperature. However, the absolute yield of nitrobenzene is still higher than at higher temperatures.
- 4) With the addition of oxygen, the reaction goes to completion in a bit more than 2 hours. This is consistent with literature, i.e., that oxygen acts as catalyst.
- 5) Even without illumination, the nitration of benzene is observed and the lower the temperature, the higher the conversion. As the temperature decreases, the equilibrium between dinitrogen tetroxide and nitrogen dioxide favors the former.
- 6) Increasing the fraction of oxygen further will shorten the time for completing the reaction, but also reduces the absolute amount of benzene present in the system, already limited by its partial pressure.
- 7) Increasing the pressure at higher temperatures (above boiling point of benzene) will increase the yield but deemed not useful for the practical application.
- 8) Increasing the pressure at low temperatures is dictated by the vapor pressure of benzene at that given temperature. As such, there is some room from improving the yield, but at a certain point benzene will start to condense (saturation).

It seems that the abundance of benzene in the vapor phase is not a limiting factor for the nitration, as the amount of benzene in the vapor phase is limited by the partial pressure of benzene and the yield increases with decrease of reaction temperature.

As high yields are observed at 0 °C and as the equilibrium between dinitrogen tetroxide and nitrogen dioxide shifts to the former at such low temperature, it is assumed that dinitrogen tetroxide presence may favor the nitration.

The experimental results are promising regarding yield and selectivity; a reaction time of 2 hours is still too long for a practical application, and the introduction of a catalyst is deemed necessary.

From a practical (industrial scale) point of view, an NO₂/benzene ratio close to unity, a reaction taking place near room temperature, and in the presence of air instead of oxygen, is desirable. Such conditions will limit utility costs and avoid air separation units.

4.3 Task 2: Catalyzed photochemical solventless nitration of benzene

4.3.1 Catalyst testing

The effect of the addition of catalysts was studied using the setup shown in Figure 10, introducing light via 7 parallel glass rods. Reference experiments were performed for comparison of this setup with the stainless-steel reactor applied in Task 1. Using the optimized conditions mentioned in Table 2, the influence of temperature, reaction time, illumination and catalyst on the nitrobenzene yield was investigated, see Table 3.

Table 3. Influence of temperature, reaction time, illumination by 365nm LED and catalyst type on the nitrobenzene yield using a NO₂:benzene:O₂ molar ratio of 10:1:16.

| Experiment # | Temperature [°C] | Reaction time [min] | Illumination | Catalyst | Yield nitrobenzene (mole%) |
|--------------|------------------|---------------------|--------------|------------------------|----------------------------|
| 2-1 | 20 | 30 | No | n.a. | 12 |
| 2-2 | 20 | 120 | No | n.a. | 52 |
| 2-3 | 20 | 30 | Yes | n.a. | 33 |
| 2-4 | 20 | 30 | Yes | Chromium powder | 33 |
| 2-5 | 20 | 30 | Yes | NH ₄ -ZSM-5 | 48 |
| 2-6 | 20 | 30 | Yes | H-ZSM-5 | 39 |
| 2-7 | 20 | 30 | Yes | Niobic acid* | 69 |
| 2-8 | 20 | 30 | Yes | Niobic acid** | 70 |
| 2-9 | 20 | 5 | Yes | Niobic acid** | 37 |
| 2-10 | 20 | 5 | Yes | Niobic acid** | 50 |
| 2-11 | 90 | 30 | Yes | n.a. | 5 |
| 2-12 | 90 | 60 | Yes | n.a. | 3 |
| 2-13 | 90 | 30 | Yes | Chromium powder | 23 |
| 2-14 | 90 | 30 | Yes | NH ₄ -ZSM-5 | 17 |
| 2-15 | 90 | 30 | Yes | H-ZSM-5 | 28 |
| 2-16 | 90 | 30 | Yes | Niobic acid* | 21 |
| 2-17 | 90 | 30 | Yes | Niobic acid** | 15 |

* Niobic acid pretreated at 120 °C for 4 hours in a muffle oven.

** Niobic acid pretreated at 300 °C for 4 hours in a muffle oven.

At 90 °C, only low nitrobenzene yields (< 6 mole%) were observed after 30-60 minutes. Upon application of different catalysts, the nitrobenzene yields increased to 15 – 28 mole% after 30 minutes.

Addition of a chromium catalyst at 20 °C did not affect the nitrobenzene yield while addition of zeolite catalysts (H-ZSM-5, NH₄-ZSM-5) at 20 °C increased the nitrobenzene yield by a factor 1.2 to 1.5. Upon niobic acid addition, the nitrobenzene yield at 20 °C increased to 70 mole% after 30 minutes.

Since high nitrobenzene yields were obtained after 30 minutes at 20 °C upon niobic acid application, the reaction time was further reduced to 5 minutes. This yielded 37 and 50 mole% in two sequential experiments. The reason for the previously not observed large deviation is

likely related to the short reaction time compared to the time required for work-up of the reaction mixture. The reaction time was defined as the time during which the reactant was present at the reaction temperature and illuminated with a LED. The reaction was “aborted” by switching off the LED and cooling the flask in an ice bath. However, as the reaction also proceeds at 0 °C without illumination (see Table 2), it could proceed up to the moment that the reaction mixture was analyzed by NMR and hence the actual reaction time will be longer and less defined.

In the stainless-steel reactor, catalysts were tested as well (see section 3.3.2). All tests were performed at room temperature and with a fixed reaction time of 1 hour. The effect of different catalysts on the nitrobenzene yield was investigated, see Table 4.

Table 4. Effect of different catalysts on the nitrobenzene yield (in mole%). Experiments were performed at room temperature for 1 hour.

| Catalyst | NO ₂ :benzene molar ratio of 10:1 | | NO ₂ :benzene:O ₂ molar ratio of 10:1:16 | |
|-------------------|---|--------------|---|--------------|
| | No light | Illumination | No light | Illumination |
| No catalyst | 2 | 13 | 16 | 58 |
| Aluminum silicate | 3 | 10 | 16 | 69 |
| WO ₃ | 9 | 16 | 58 | 84 |
| ZrO ₂ | 2 | 12 | 20 | 56 |
| Nafion | 3 | 12 | 56 | 60 |
| ZSM-5 | 6 | 10 | 60 | 67 |

4.3.2 Discussion and Conclusions

As a systematic research into the best catalyst was not intended for this project, the catalysts tested were based on literature (see Section 1.2) and give clear indications that the reaction time can be significantly reduced. For a practical application, based on flow chemistry, a reaction time in the order of maximum a few minutes would make the business case achievable for this type of reactions. As with the non-catalyzed experiments (see Section 4.2), an increase in the reaction temperature has a detrimental effect on the yield of nitrobenzene. Of all catalysts tested, the zeolite/aluminum silicate-based catalysts show some improvement in reducing the reaction time, whereas niobic acid and tungsten oxide show significant improvements. Based on a better understanding of the reaction mechanisms a more dedicated search for catalysts will be possible. Based on literature data there are indications that specific catalysts exist for selectively synthesizing higher nitrated benzene (dinitrobenzene, trinitrobenzene). In the present work traces of dinitrobenzene were found (less than 1 percent) using NMR analysis.

4.4 Task 3: Solventless nitration of TO to NTO

4.4.1 Introduction

For the solventless photonitration of 1,2,4,-triazole-5-one (TO) to 3-nitro-1,2,4,-triazole-5-one (NTO) a fluidized bed reactor setup was used. First the characteristics of the solid TO powder are described, followed by initial nitration reactions in the glass reactor.

4.4.2 TO characteristics.

TO was, as received from Sigma-Aldrich, placed in the reactor and an attempt was made to fluidize the powder. Upon feeding a $1 \text{ L min}^{-1} \text{ g}^{-1}$ gas flow through the bed, channel formation occurred. This is generally an indication that the particles are too small and that the attractive forces between the particles cannot be overcome by the fluidizing gas [20]. Initially a P1 glass filter (max. pore size $100\text{-}160 \mu\text{m}$) was present in the reactor. To obtain a higher pressure drop across the glass filter and hence a more homogeneous gas distribution across the cross-section of the bed, reactors were acquired with a P3 filter (max. pore size $16\text{-}40 \mu\text{m}$) and a P4 filter ($10\text{-}16 \mu\text{m}$). Also, with these filters channel formation occurred in the reactor bed. To obtain a more homogeneous distribution of the TO particle size, it was sieved to three fractions: $< 63 \mu\text{m}$, $63\text{-}125 \mu\text{m}$ and $> 125 \mu\text{m}$. The best, albeit not ideal, fluidization was obtained for the $63\text{-}125 \mu\text{m}$ fraction.

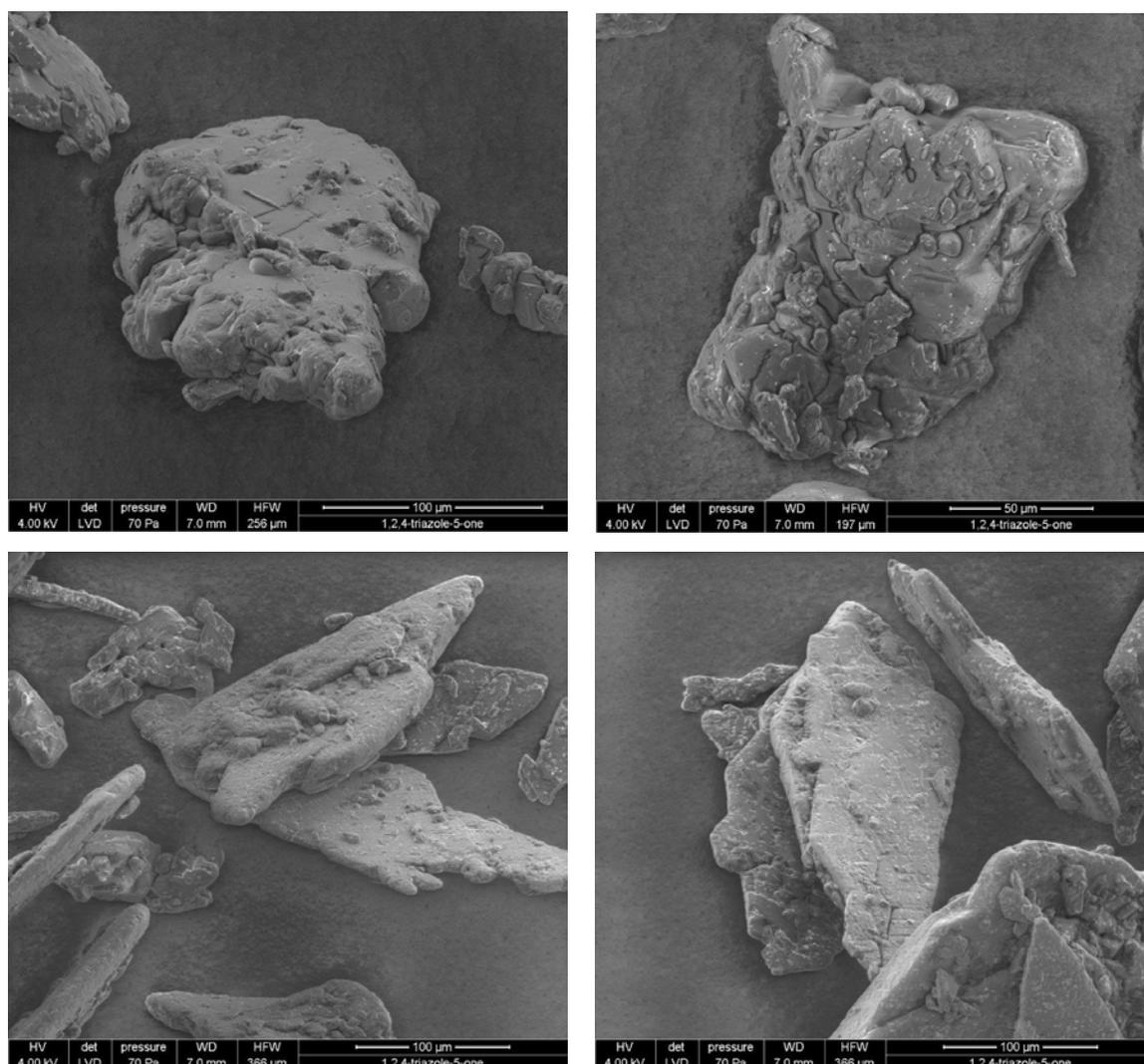


Figure 18. Scanning electron microscopy images of 1,2,4-triazole-5-one.

The origin for the non-ideal fluidization behavior was further studied using scanning electron microscopy (SEM). The TO particles appeared to be irregularly and anisotropically shaped, see Figure 18. The non-spherical shape affects the fluidization properties. The flat particles are more prone to interparticle attraction forces, promoting channel formation.

The observed particle shape is assumed to be the preferential morphology after synthesis. Since the synthesis procedure is expected to be similar for all potential suppliers and none of them was able to supply any information on particle size and morphology, the only method for obtaining TO particle with a more favorable shape might be controlled recrystallization.

4.4.3 Proof of principle using the batch reactor.

The setup applied for the catalyzed photochemical nitration of benzene (Figure 10) was used for a proof of principle experiment for the nitration of TO by NO₂. In the flask 0.25 g TO (3 mmol, fraction < 63 μm) was placed. The flask was evacuated, 240 mL O₂ was added and NO₂ was dosed to 0.9 bara (~ 6 mmol NO₂ present, ratio NO₂ : O₂ = 10 mole : 16 mole). The reaction mixture was illuminated via 7 glass rods for 60 minutes. The solid reaction mixture was dissolved in D₂O and analyzed using ¹H and ¹³C NMR. Based on the decrease of the TO signal, the NTO yield was calculated to be roughly 20 mole%.

Table 5. Experimental results of the nitration of TO to NTO in the batch reactor as a function of temperature and reaction time.

| Experiment | Temperature [°C] | Time [min] | Ratio NO ₂ :O ₂ [-] | Yield NTO [mole%] | Remark |
|------------|------------------|------------|---|-------------------|-------------------------|
| 3-1 | 20 | 60 | 0.6 | 21 | |
| 3-2 | 20 | 60 | 0.6 | 22 | |
| 3-3 | 20 | 60 | 1 | 19 | |
| 3-4 | 20 | 60 | 0.6 | 20 | Niobic acid as catalyst |
| 3-5 | 0 | 60 | 1.2 | 23 | |
| 3-6 | 60 | 60 | 0.6 | 25 | |
| 3-7 | 20 | 15 | 0.7 | 14 | |

As can be seen from Table 5, the nitration of TO to NTO is technically feasible. Due to the improper fluidization, the conversion is low. Also, the interaction between powder, gas and catalyst is not optimal in this configuration. It is likely that with optimization the conversion will be higher and with that the reaction time will come down to acceptable levels.

Since NTO could not be observed using ¹H NMR, the reaction product was also analyzed using infrared spectroscopy using a Thermo Nicolet 6700 ATR-FTIR spectrometer, see Figure 20. Clearly the spectrum of the reaction product, obtained by LED illumination of TO in the batch reactor for 1 hour, shows a mixture of TO and NTO, providing evidence that the reaction product is NTO.

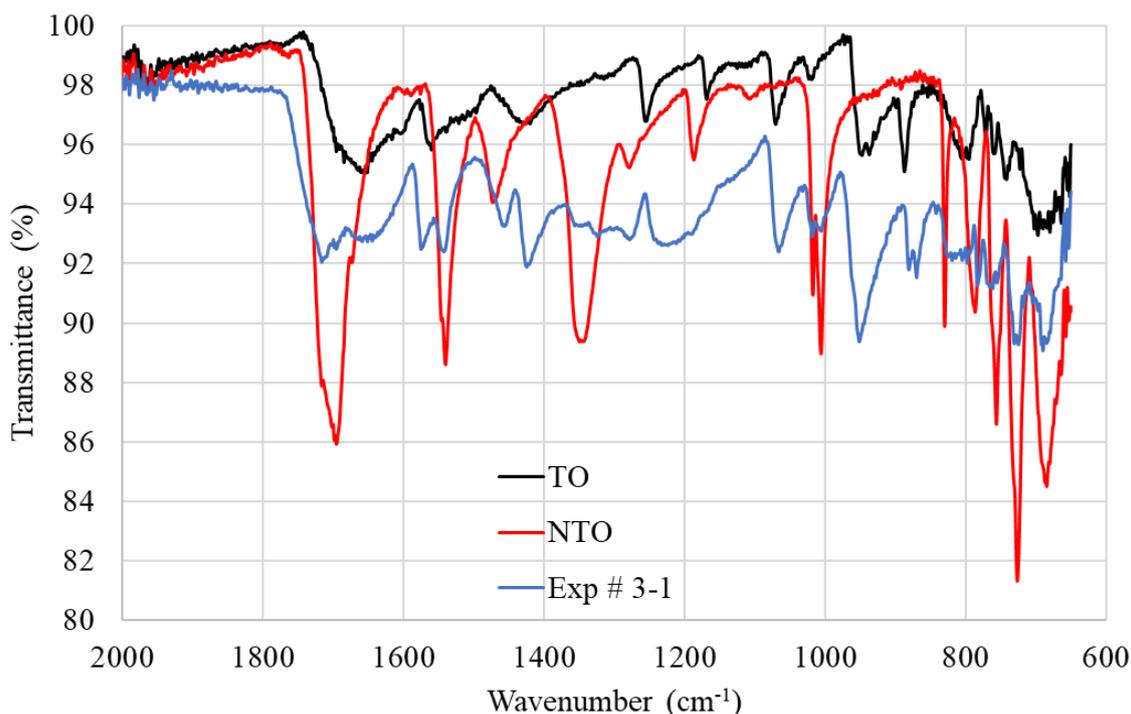


Figure 19. FTIR spectra obtained using ATR-FTIR on a Thermo Nicolet 6700 spectrometer for pure TO (black), pure NTO (red) and a reaction mixture after 1 hour of illumination in a flask (Exp # 3-1, blue).

4.4.4 Fluidized bed experiments

Experiments were conducted for the nitration of TO by NO_2 . Although small particles are desired for a higher probability of full nitration (largest surface to volume ratio), a first nitration experiment was conducted using the 63-125 μm TO fraction in a reactor with a P4 glass filter to obtain the best fluidization achievable. 1 g of TO was placed in the reactor, fluidized using a 1 L min^{-1} flow of 10 vol% NO_2 in N_2 and illuminated for 60 minutes. It should be noted that the bottles with NO_2 in N_2 also contain O_2 to avoid the decomposition of nitrogen dioxide. As such, oxygen as catalyst was present by default in the ratio $\text{NO}_2 : \text{O}_2 = 1 : 1$. Although this is not the optimum ratio, for showing the principle of nitration by fluidization no additional complex measures were taken to add oxygen to the system.

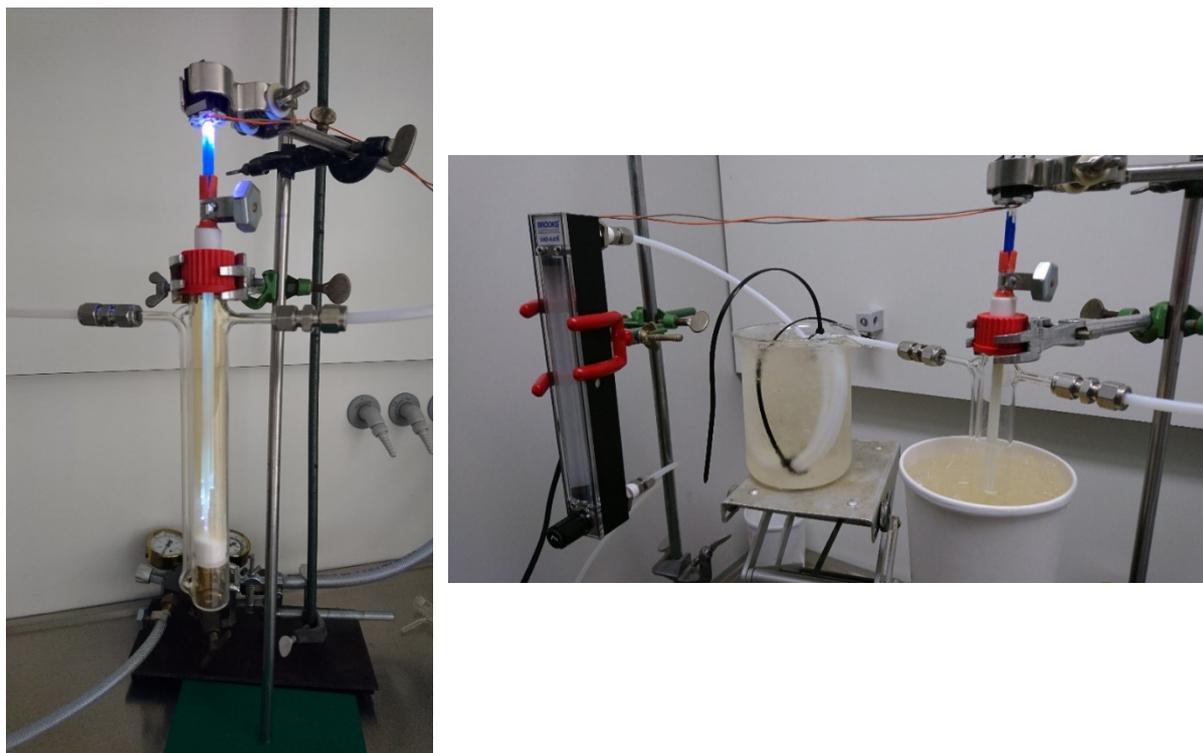


Figure 20. Part of the setup for fluidized bed nitration of TO (left) and setup for experiments at 0 °C including pre-cooling of the nitrating agent in ice (right).

The results obtained with the fluidization reactor are given in Table 6. For the experiments at 20 °C using 1 g of TO (Exp #3-8 to #3-10) a significant deviation in the NTO yield was observed. This is related to the difficult and non-consistent fluidization of the bed, regularly showing formation of channels or preferential flow along the reactor wall, see Figure 21. As mentioned in section 4.4.2, the formation of channels through the TO bed and/or the formation of a bypass of the TO bed along the fluidized bed reactor, significantly reduces the surface area of TO available for nitration, resulting in the low yields observed. The fluidization could be aided by giving the reactor a vibration. This temporarily caused the TO bed to form a homogeneous mixture, but after a fraction of a second the channel formation appeared again. Although the nudging of the reactor could have been repeated to increase the yield of NTO, it was not considered as in a practical situation this would not be preferable either, especially at larger scales.

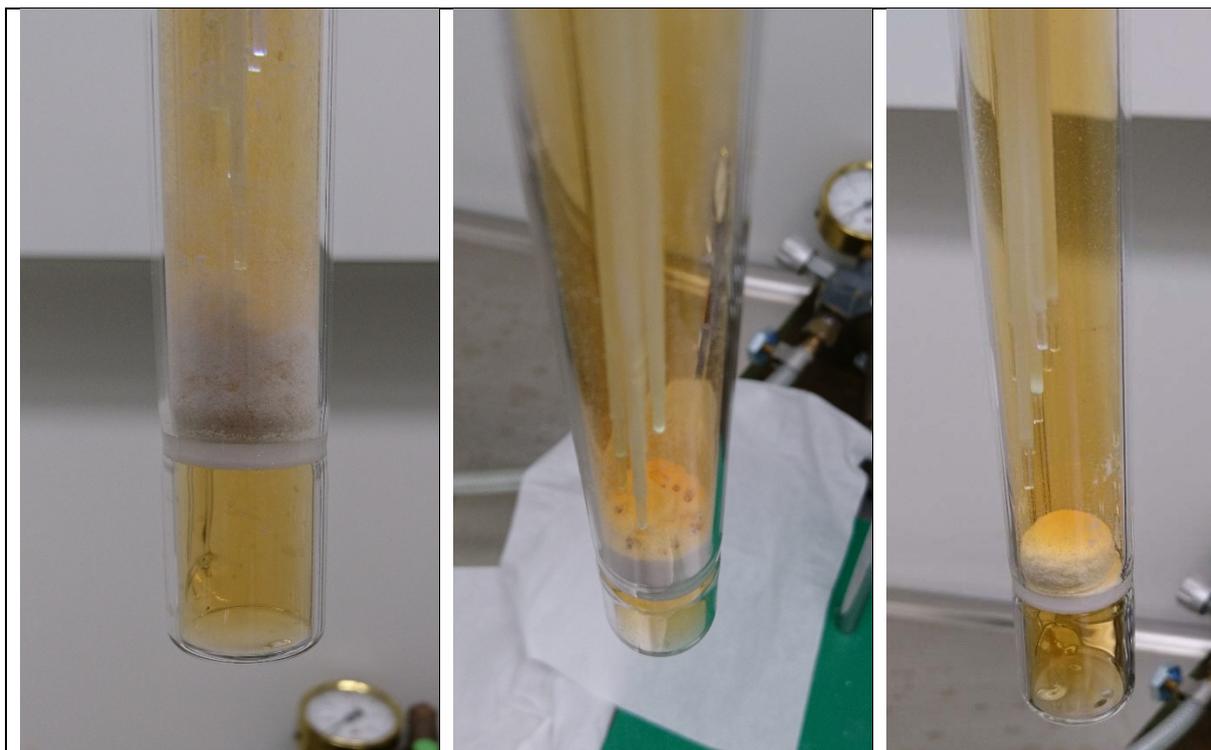


Figure 21. TO bed during fluidized bed experiments: fluidization of TO (left), formation of channels in TO bed (middle) and preferential flow along the reactor wall (right).

Since operation at low temperature was found to stimulate nitration of the benzene (Section 4.2.2), nitration of TO was also explored at 0 °C. Upon cooling the reactor in an ice bath, the TO bed was seen to shrink and no visually discernable fluidization occurred, leading to a reduced NTO yield at 0 °C. To stimulate formation of N_2O_4 , precooling of the nitrating agent was also explored (Figure 20, right). The cooling of the NO_2 , however, did not increase the NTO yield, again due to bad fluidization properties of the TO bed. Operation at 40 °C was found to reduce the NTO yield, which is in agreement with the results found with benzene (Section 4.2.2).

In the fluidization experiments significantly lower NTO yields were observed than in the batch reactor (Table 5). This is likely related to the reduced contact between the nitrating agent and the TO due to the limited penetration of NO_2 in the 63-125 μm particles and in the non-ideally fluidized TO bed. To overcome this, experiments were also performed using less TO and using TO particles < 63 μm . Fluidization was found to be absent and the NTO yield was found to be reduced for both experiments (Exp # 3-14 and 3-15, see Table 6).

Table 6. Fluidized bed nitration of TO to NTO. Experiments performed at room temperature for 1 hour with a flow rate of 1 L min⁻¹, 1 g TO, particle size distribution of 63-125 μm, and a NO₂:O₂ ratio of unity, unless stated otherwise.

| Experiment | NTO yield (mole%) | Remark |
|------------|-------------------|--|
| 3-8 | 10 | |
| 3-9 | 10 | |
| 3-10 | 5 | |
| | | |
| 3-11 | 5 | Reaction at 0 °C |
| 3-12 | 5 | 0.2 g TO, reaction at 0 °C, pre-cooled gas |
| 3-13 | 1 | Reaction at 40 °C |
| | | |
| 3-14 | 2 | 0.2 g TO |
| 3-15 | 5 | TO particle size < 63 μm |

Some of the more promising catalysts found with task 2 (see Section 4.3) were tested in the fluidized bed test setup. It is known that for improving the fluidization characteristics [21], it is possible to add an inert material, such as glass beads. This will improve the fluidization of the bed by, for instance, inhibiting or reducing the formation of channels as seen in Figure 21 due to a more homogenous distribution of the gaseous fluidization agent, in this case nitrogen dioxide. Instead of using glass beads it was decided to use the catalyst particles for this purpose. For the contact between the catalyst and TO particles, in combination with the presence of NO₂, this configuration will not be significantly different to the situation where the catalyst particles are adhered to the glass rods and immersed in the fluidized TO bed. Addition of 0.5 or 1 g niobic acid to 1 g TO enhanced the fluidization of the bed. However, it did not enhance the NTO yield significantly (Table 7). Addition of a small amount of niobic acid (TO:catalyst ratio 5:1 by weight) or the application of a TO fraction < 63 μm reduced the NTO yield, probably due to reduced fluidization and consequently reduced TO – NO₂ interaction. Also operation at 0 °C and the application of ZrO₂ or WO₃ as catalysts did not improve the yields.

Table 7. Fluidized bed nitration of TO to NTO. Experiments performed at room temperature for 1 hour with a flow rate of 1 L min⁻¹, 1 g TO, particle size distribution of 63-125 μm, TO:catalyst ratio 1:1 by weight and a NO₂:O₂ ratio of unity, unless stated otherwise.

| Experiment | Catalyst | NTO yield (mole%) | Remark |
|------------|------------------|-------------------|----------------------------------|
| 3-16 | Niobic acid | 8 | TO:catalyst 2:1 |
| 3-17 | Niobic acid | 2 | TO:catalyst 5:1 |
| 3-18 | Niobic acid | 9 | |
| 3-19 | Niobic acid | 4 | TO particle size < 63 μm |
| | | | |
| 3-20 | Niobic acid | 1 | Reaction at 0 °C, pre-cooled gas |
| | | | |
| 3-21 | ZrO ₂ | 5 | TO:catalyst 5:1 |
| 3-22 | WO ₃ | 3 | TO:catalyst 5:1 |

To overcome the limited interaction between TO and the nitrating agent due to the non-ideal fluidization behavior, some experiments were performed with the reactor in fixed bed mode, i.e., the nitrating agent flowing top-down through the TO bed. Although this configuration is all but fluidization, it does prevent the preferential formation of channels and the nitrogen dioxide will be forced through the entire bed, in the hope to increase the total contact area between nitrogen dioxide and TO. The experiments were performed with a reduced gas flow (0.15 L min^{-1}) to prevent pressure build-up in the reactor due to pressure drop over the TO bed.

The experiment was performed in duplo (Exp #3-23 and 3-24) and based on NMR analysis, NTO yields of 19 and 5 mole%, respectively, were determined see Table 8. To investigate whether this difference was related to an artefact during the NMR sample preparation and analysis, the product of these experiments was also analyzed using ATR-FTIR spectroscopy. Reaction mixtures of Exp #3-23 and 3-24 were analyzed using a Thermo Nicolet 6700 FTIR spectrometer. The higher NTO yield in experiment # 3-23 was confirmed by FTIR analysis, as clearly observed from the more pronounced NO_2 stretch band around 1500 cm^{-1} (Figure 22). The significantly higher yield for experiment #3-23 indicates that when the fluidization of TO is further optimized, higher yields are possible.

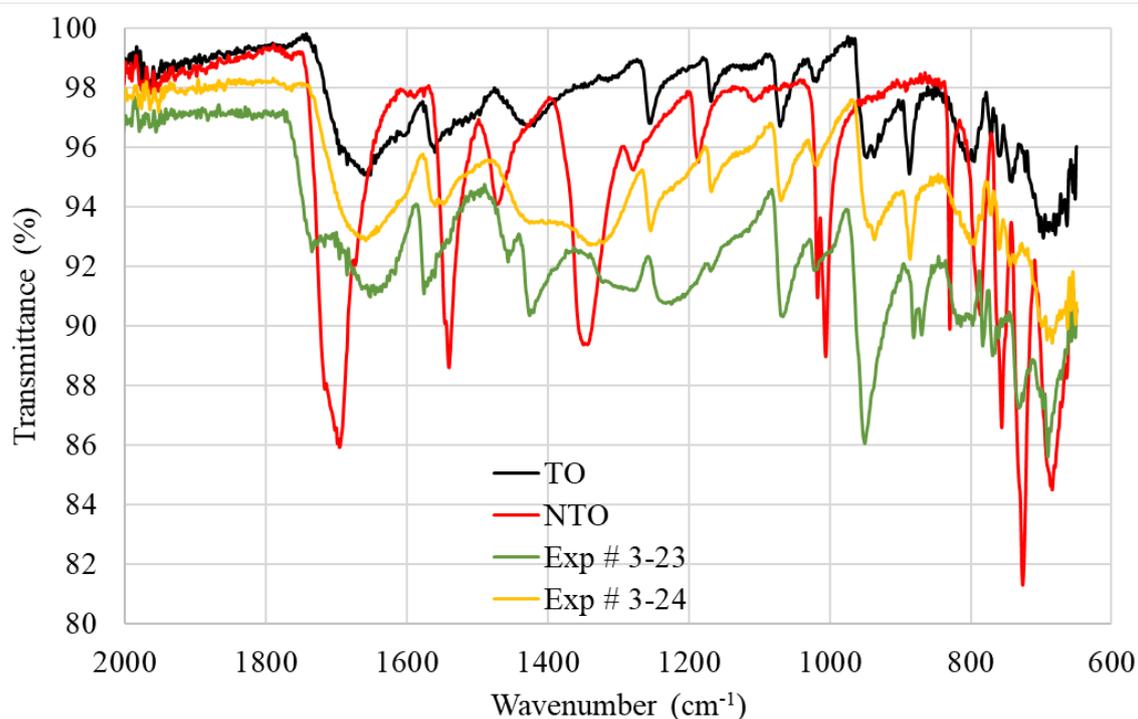


Figure 22. FTIR spectra obtained using ATR-FTIR on a Thermo Nicolet 6700 spectrometer for pure TO (black), pure NTO (red) and the reaction mixtures after 1 hour of illumination during a fixed bed nitration at room temperature.

Please note that due to the limited flow used in the fixed bed configuration (to avoid overpressure in the glass reactor), while keeping the total experimental time the same, the amount of NO_2 seen by the TO particles is a factor 7 lower compared to the fluidized bed experiments.

To enhance the NTO yield, the fixed bed system was also operated at $0 \text{ }^\circ\text{C}$, and application of less TO and smaller TO particles was explored. For all experiments NTO yields of 4 to 6 mole%

were determined after 60 minutes. The addition of niobic acid as catalyst increased the NTO yield 9 mole%.

Table 8. Fixed bed nitration of TO to NTO. Experiments performed at room temperature for 1 hour with a flow rate of 0.15 L min⁻¹, 1 g TO, particle size distribution of 63-125 μm, and a NO₂:O₂ ratio of unity, unless stated otherwise.

| Experiment | NTO yield (mole%) | Remark |
|------------|-------------------|---|
| 3-23 | 19 | |
| 3-24 | 5 | |
| 3-25 | 5 | 0.2 g TO |
| 3-26 | 6 | 0.2 g TO, Reaction at 0 °C, pre-cooled gas |
| | | |
| 3-27 | 4 | TO particle size < 63 μm |
| 3-28 | 5 | 0.2 g TO, TO particle size < 63 μm |
| 3-29 | 9 | 0.5 g TO, TO particle size < 63 μm, 0.5 g niobic acid as catalyst |

It should be noted that the nitrogen dioxide was delivered in 50-liter cylinders from Air Liquide. To ensure the stability of the nitrogen dioxide gas inside the cylinders, the gas supplier added oxygen. Without this oxygen added, the nitrogen dioxide may decompose. However, the ratio of nitrogen dioxide to oxygen is fixed in this way by the supplier. The ratio between these two gasses is not the optimum ratio as found during the execution of work package 1 (see section 4.2). Additional pure oxygen and/or nitrogen dioxide can be added to bring the concentration more in line with the optimum concentration ratio mentioned in section 4.2. In the ideal case this will be done by the supplier of the gas cylinders.

4.4.5 Conclusions

It was shown that it is technically possible to produce NTO by the nitration of TO without the use of solvents and/or liquid acids in a fluidized bed configuration. A further optimization of the reaction conditions is needed to increase the yield and reduce the reaction time to acceptable levels. To improve the fluidization characteristics, the morphology of the TO particles needs to be adjusted such that the interparticle attraction forces are overcome to such an extent that a homogeneous fluidized bed can be generated, which is difficult to achieve with flat, pancake-like particles.

4.5 Task 4: Microwave-assisted solventless nitration

4.5.1 Experiments in standard microwave reactor.

To assess whether microwave irradiation would benefit the nitration reactions and to avoid the costly construction of an intrinsically safe setup using the fluidized bed reactor, experiments were conducted in (batch) vials using a commercially available microwave reactor, see Section 3.5.

For the nitration of benzene, a mixture of NO₂, O₂ and benzene was irradiated for 10 minutes using microwaves (~100 W), allowing the temperature to rise to 40 °C. For comparison an identical mixture was prepared which was not irradiated with microwaves but placed in an oven at 40 °C for 10 minutes to mimic the reaction conditions in the microwave, except for the

microwave radiation. The influence of catalysts was tested by the addition of 0.05 g of niobic acid catalyst.

Microwave-assisted nitration of TO was tried using the most reactive gas mixture identified in Task 1 (section 4.2). In a 31 mL microwave tube NO₂ and O₂ were added to 0.05 g TO (< 63 μm). After microwave irradiation for 10 minutes at 40 °C, the reaction product was dissolved in D₂O and after addition of an internal standard analyzed using ¹H NMR.

Table 9. Effect of 10 minutes microwave radiation on the nitration of benzene (BZ) and 1,2,4,-triazole-5-one (TO). Please note that the minimum operating temperature of the microwave reactor is 40 °C.

| Substance | Temperature [°C] | Ratio BZ:NO ₂ :O ₂ or NO ₂ :O ₂ [-] | Catalyst | Yield [%] | |
|-----------|------------------|---|------------------|----------------------------|--------------------------|
| | | | | With microwave irradiation | No microwave irradiation |
| Benzene | 20 | 1:11:18 | Niobic acid | - | 91 |
| | 40 | 1:11:16 | Niobic acid | 92 | - |
| | 20 | 1:11:18 | - | - | 5 |
| | 40 | 1:13:20 | - | 5 | - |
| TO | 40 | 11:17 | - | 10 | 8 |
| | 40 | 11:17 | - | 11 | 9 |
| | 40 | 11:17 | - | 13 | 5 |
| | 40 | 11:17 | Niobic acid | 2 | 1 |
| | 40 | 11:17 | WO ₃ | 7 | 8 |
| | 40 | 11:17 | ZrO ₂ | 6 | 7 |

As can be seen from Table 9, microwave radiation has no influence on the nitration reaction. Please note that the yield with benzene and niobic acid is high. Although the experiment takes 10 minutes in the microwave reaction, before the sample can be analyzed the nitration reaction has already progressed to almost completion. As such this is an artefact of the experimental procedure and not related to the microwave reactor.

As mentioned previously, in this setup the LED system cannot be introduced, but for the assessment of the effectiveness of the microwave radiation, that is not relevant. If microwave radiation has an effect on the conversion of the nitration reaction, the combination of both LED and microwave radiation is not likely to intervene with each other in a detrimental way for the yield.

4.5.2 Conclusions

Microwave radiation has no effect on the nitration reaction of benzene to nitrobenzene or that of the conversion of TO to NTO in the presence of NO₂ as the nitrating agent.

5 Conclusions and recommendations

Using a light reactor it was shown to be possible to nitrate gaseous benzene to nitrobenzene and solid 1,2,4-triazole-5-one (TO) to nitro-1,2,4-triazole-5-one (NTO) using a solventless photochemical nitration technique. As nitrating agent gaseous nitrogen dioxide was used.

The nitration of benzene was performed with 100% selectivity and close to 100% conversion under optimized conditions. The addition of a catalyst significantly reduced the reaction time to reach nearly 100% conversion from several hours to the minutes range.

The nitration of 1,2,4-triazole-5-one, using a fluidized bed, was also successfully performed with 100% selectivity, albeit with a lower yield of 20%. This was mainly due to the morphology of the TO particles (disks), hampering the homogeneous fluidization of the TO bed.

For both the nitration of benzene and TO it was shown that oxygen acts as a catalyst for the nitration reaction. It was shown that normal air can be used for this purpose, without any detrimental effect on the products formed. i.e., not other species are formed in case nitrogen (from air) is present.

Microwave radiation does not affect the conversion of benzene to nitrobenzene or that of 1,2,4-triazole-5-one (TO) to nitro-1,2,4-triazole-5-one (NTO) with the use of nitrogen dioxide as the nitrating agent.

The following recommendations can be made.

With the nitration of benzene, mononitrobenzene was the major product. It is known that with proper catalysts, the nitration process can be controlled to selective produce multi-nitrated compounds. As a step forward, the continuous nitration of toluene to trinitrotoluene (TNT) is preferred, for which the most efficient catalyst to effectuate the nitration of toluene with three nitro groups needs to be identified. When successful, the entire waste stream (so-called 'red water') that plagues the traditional TNT production process can be circumvented.

Due to the unfavorable fluidization characteristics of TO it is recommended to improve the morphology of this material. By creating a more spheroid or cubical form, the fluidization of TO will improve and with that the yield of NTO will improve. It may be an intrinsic feature of TO that it cannot be produced in a shape other than the observed pancake-like morphology. In that case a more complex fluidized bed with for instance baffles or a swirled inlet flow can be considered to break up or reduce the occurrence of the formed channels.

Alternatively another solid substrate can be considered that has a more favorable morphology to aid the fluidization process. An example is for instance hexamine that serves as a precursor for the formation of RDX/HMX. It should be noted that hexamine slowly sublimates and as such downstream of the bed other measures need to be taken to avoid hazardous situations.

As an expansion of the working envelope of the light reactor it is recommended to use a liquid substrate. This will be less complicated than the fluidization of a powdered material, as the design of a bubble column is more straightforward and is not hampered by morphology issues (as a liquid is not characterized by morphology). As with the fluidized bed, the gas used for creating the bubble column will be the nitrogen dioxide in nitrogen, stabilized with oxygen. A

potential candidate for this is glycerol. It should be noted that nitroglycerin (NG) is susceptible for slight decomposition under the influence of light. Prior to considering the glycerin/nitroglycerin option, the susceptibility for decomposition of NG at 365 nm, the wavelength used to activate nitrogen dioxide, needs to be determined. It may be possible, though, that with a proper catalyst in combination with the most suitable temperature, the activation with light may not be needed. In case this does not pose a problem, the nitration of glycerin to nitroglycerin can be easily scaled up in a continuous fashion and the business case is likely positive, as the solubility of nitroglycerine in glycerin is very low. This means that the separation is extremely simple: NO_2 in nitrogen (or air) is bubbled through glycerin, the nitrogen dioxide is activated by light and upon degassing, two separate liquids appear. The non-reacted glycerin can be recycled.

As a concluding remark, for a practical processing plant, it is deemed highly favorable that the reaction can take place at room temperature (no utility costs) as shown in this work and that air can be used as the oxygen containing catalyst (no air separation unit required). For a practical application, based on flow chemistry, a reaction time in the order of maximum a few minutes would make the business case achievable for this type of reactions.

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