



Microwave-Assisted Synthesis of Para-Nitrophenol Using Calcium Nitrate

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ABSTRACT

Conventional process of nitrating phenolic compounds involves the use of excess corrosive reagents that impose environmental threats. Rapid and environmentally friendly microwave-assisted nitration of phenol has been employed to limit the use of corrosive nitric acid and sulfuric acid. In this study, phenol is reacted to calcium nitrate and acetic acid, which served as nitrating agents. The solution is irradiated under microwave to complete the nitration process. This microwave-assisted-synthesis is a rate-enhanced process that showed complete nitration in a short reaction time of 1 min with a high yield of 89%. Bands of phenyl ring, OH, CO, and nitro groups observed in the FTIR spectra correspond to the vibration modes of *para*-nitrophenol. GCMS analysis showed a retention time of 7 min for the product with 139m/z base peak with matches that confirms the synthesis of *para*-nitrophenol. This microwave-assisted method can be employed as an efficient, environmentally safe, and rapid alternative nitration method for the synthesis of *para*-nitrophenol.

Keywords: Microwave-assisted, Nitration, *para*-Nitrophenol, Nitrating agents.

INTRODUCTION

Para-nitrophenol or 4-nitrophenol belongs to the group of phenolic compounds where a nitro group is opposite the hydroxyl group in the benzene ring. Among the various applications of 4-nitrophenol are its use in the pharmaceutical industry as an intermediate in paracetamol synthesis and as precursors for phenetidine and acetophenetidine¹. It is also synthesized for its application in dye and pigment production as well as in plastics

formulation and polymer engineering². Manufacturer of agrochemical products use *para*-nitrophenol as a raw material in fungicides and is an evident degradation product of pesticides such as parathion and fluoridifen^{3,4,5}.

Nitrophenols are not naturally occurring and hence are synthetically synthesized for a variety of uses. Traditional methods of synthesis follow the mechanism of nitration of aromatic compounds, which uses liquid mixtures of nitric acid and sulfuric



acid. Traditional synthesis yields a mixture of *ortho*- and *para*-nitrophenols due to the low regioselectivity of the method. Another drawback is the production of acid wastes from the excessive use of strong acid reagents⁶. Alternative nitration procedures were also established to lessen the production of acid wastes and to enhance the regioselectivity of the reaction. The use of metal catalysts and molecular frameworks such as zeolites⁷, clayfen, claycop and clayzic⁸, metal nitrates⁹, and solvent-free reactions¹⁰ were being explored as possible procedure towards green chemistry and regioselectivity of the nitration reaction. Another method is the microwave-promoted nitration, which uses nitrate salts, less corrosive acids, proceeds by a rapid reaction time, with recorded high regioselectivity and higher product yield^{11,12}.

In this study, phenol was nitrated to yield *para*-nitrophenol. The nitration process was carried out in a microwave-assisted set-up using calcium nitrate and acetic acid as nitrating agents. This nitration method was completed in a minute with the use of commonly available reagents that are less toxic and less corrosive compared to the traditional method.

MATERIALS AND METHODS

Reagents and Instruments

Reagents used in this study, including phenol, calcium nitrate, glacial acetic acid, and methanol, are all reagent grades. A Gas Chromatography-Mass Spectrometry (GC-MS) TQ4080 (Shimadzu) and a Spectrum Two FT-IR Spectrometer (PerkinElmer) were used to characterize the synthesized product.

Microwave-assisted Nitration

The microwave-assisted synthesis of nitrophenol was based on literature with modifications¹³. Briefly, 1.0 mL phenol, 2.0 g Calcium nitrate, and 5.0 mL glacial acetic acid were stirred in an Erlenmeyer flask. The mixture was covered and placed at the center of a microwave model MWP305ES with 900W output at 2450MHz. The microwave-assisted nitration reaction was carried out by irradiating the reaction mixture for 1 minute. A darkening of the mixture was observed after the reaction was complete. This was then allowed to cool and refrigerated prior to characterization experiments.

FTIR Characterization

The reaction product was analyzed using attenuated-total reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). The IR spectra of the product were recorded using a PerkinElmer Spectrum Two FT-IR Spectrometer.

GC-MS Characterization

The reaction product was characterized using gas chromatography-mass spectrometry. A drop of the reaction product was mixed with 2 μ L methanol before the analysis. The analysis was performed using Shimadzu GC-MS TQ4080 with a Durabond DB-5MS GC column (0.25mm x 30m). Helium was used as the carrier gas with a flow rate of 0.84mL/minute. The injector temperature was 260°C and a temperature program was used for the analysis. The initial temperature was 90°C held for 1 min; increased at 10°C/min to 150°C held for 2 min; increased at 15°C/min to 220°C for 2 min and increased at 20°C/min to 290°C held for 6 minute. Splitless mode of injection was applied for all injections. The detector scanned in a mass range of m/z 40- 500. The identity of the product was matched with the MS library of compounds.

RESULTS AND DISCUSSION

Synthesis and FTIR Characterization

This study employed the use of microwave irradiation instead of the traditional process, which involves heating under reflux. This technique is found to be useful in the nitration process as the reaction proceeded at a much faster rate decreasing the reaction time from hours to just minutes. The mechanism of nitration of aromatic compounds proceeds by an electrophilic attack involving nitronium ion. Here, commonly available and environment- friendly reagents were used as nitrating agents instead of the corrosive nitric acid and sulfuric acid used in conventional nitration. Calcium nitrate reacted with acetic acid to yield calcium acetate and nitric acid, which served as the source of the nitronium ion. This then reacted with the aromatic ring of phenol and yielded the nitrophenol product with 89% yield.

The collected product was analyzed under FTIR to confirm the presence of nitrophenol.

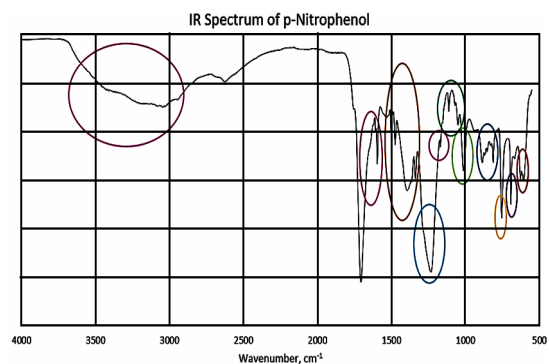


Fig. 1. IR Spectrum of p-Nitrophenol

The IR spectrum of the product in Fig. 1 showed IR peaks representing the nitro, OH, and CO groups and a phenyl ring, which are all attributes of the nitrophenol product. Corresponding frequencies to the different vibration modes of the IR bands are listed in Table 1.

Table 1: Summary of the vibration modes and corresponding IR frequencies for p-nitrophenol

Frequency, cm ⁻¹	Vibration Mode
Nitro group	
627	Scissoring NO ₂ + in-plane CH ring vib
755	Wagging NO ₂
764, 885	NO ₂ + out-of-plane CH vib
1387, 1550	NO ₂ Symmetrical + asymmetrical stretch
OH group	
692	OH torsional vib
1169	OH in-plane bend
3046-3620	OH stretch
CO group	
1232-1279	CO stretch
Phenyl ring	
1112, 1167, 1305, 1474	CH bend
1009	Ring breathing vib
1636	C=C aromatic ring vib

The band at 627 cm⁻¹ corresponds to the NO₂ scissoring and in-plane ring vibrations. Bands at 755 cm⁻¹ (wagging), 764 and 885 cm⁻¹ (out of plane vibration), and 1387 cm⁻¹ and 1550 cm⁻¹ (symmetric and asymmetric stretching) all correspond to the NO₂ vibration modes. Band at

3046-3620 cm⁻¹ corresponding to OH stretching frequencies was observed. At 1169 cm⁻¹ and 692 cm⁻¹, OH in-plane bending and torsional vibrations were noted, respectively. The CO stretch in the phenyl ring is observed as a strong IR band at 1232-1279 cm⁻¹. The rest of the phenyl ring vibrations tend to be independent of the nature of the aromatic ring substituents compared to the previously noted IR bands and frequencies¹⁴. These vibrations are the C-H bending at 1112 cm⁻¹, 1167 cm⁻¹, 1305 cm⁻¹, and 1474 cm⁻¹, the ring breathing vibration at 1009 cm⁻¹ and C=C aromatic ring vibration noted at 1636 cm⁻¹.

GC-MS Characterization

The collected sample was prepared for gas chromatography analysis without further derivatization. The chromatogram showed in Fig. 2 with the peak of the product at a retention time of 7.0 min, without the need for further derivatization of the sample. A good elution of the sample from the column is notable without the derivatization process as most studies require methylation¹⁵ and silylation¹⁶ as derivatization steps prior to GC analysis. The detector used was MS, which showed the spectra of the fragmentation of the product. Matches with the library of compounds confirm the product to be 4-nitrophenol with a 139 m/z ratio shown in Figure 2.



Fig. 2. GC-MS Chromatogram of p-Nitrophenol

CONCLUSION

This current study demonstrates a fast microwave-assisted nitration process to synthesize *para*-nitrophenol. The presented method follows a rapid reaction with the use of common reagents that are less toxic and less corrosive compared to the traditional nitration reaction. The procedure gives a high yield with high regioselectivity to *para*-nitrophenol as supported by the FTIR and GCMS characterizations. This can serve as an efficient, eco-friendly and rate-enhanced method for the small-scale preparation of *para*-nitrophenol.

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Conflict of Interest

The authors declare that there is no conflict of interest in this work with regard to publication.

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