CEM CORPORATION

APPLICATION NOTES

Atmospheric Pressure Reactions with Microwave Speed in the MARS 6 and Discover SP

MARS 6

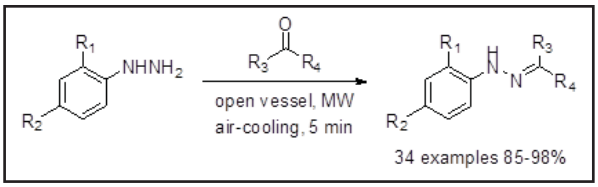
Introduction

CEM's line of microwave synthesizers, including the Discover SP and MARS 6 Synthesis units, all feature the open vessel synthesis option. This option allows for microwave chemistry to be performed at atmospheric pressure either at or below the boiling point of the solvent, enabling fast reaction times without all the potential issues of running sealed vessels. There are several advantages to performing chemistry under open vessel conditions:

- Use standard laboratory glassware
  - No special vessels required
- Larger operating scale
  - Generate more product than in sealed vessels
- No concern about pressure
  - Overall safer method than sealed vessels
- Easy access to the reaction mixture
  - Easily add or remove reagents during the reaction

N-Aryl Hydrazones

N-Aryl hydrazones can be rapidly prepared using microwave heating in open vessel mode along with simultaneous cooling to give the desired product in high yield (Scheme 1).[1] As a model reaction phenylhydrazine hydrochloride was reacted with 2-acetylpyridine in the presence of sodium acetate in 96% ethanol to give 2-(1-(2-phenylhydrazono)ethyl)pyridine. Under conventional heating at reflux the reaction took 5 hours to reach completion. Performing the same reaction in the microwave in a sealed vessel at 80 °C for 2 minutes resulted in only low yield of the product both with and without simultaneous cooling. Increasing the temperature above 80 °C also resulted in low yields, presumably due to decomposition of both the starting materials and product. When the reaction was performed under open vessel microwave heating conditions, the desired product was obtained in 98% yield after 5 minutes at 80 °C with simultaneous cooling.

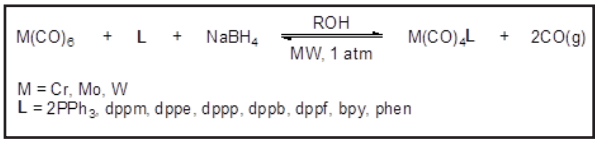


Scheme 1.
Open vessel microwave assisted synthesis of *N*-aryl hydrazones.

These optimized conditions were then used to synthesize a focused library of *N*-aryl hydrazones prepared from 4- and 2,4-(di)substituted phenylhydrazines, bearing both electron-donating (4-CH_3, 4-OCH_3) and -withdrawing (4-Cl, 4-Br, 4-CF_3, 4-NO_2, 2,4-Cl_2) groups, with 2-, 3-, and 4-acetylpyridine. This microwave protocol resulted in the preparation of *N*-aryl hydrazones in excellent isolated yields in only five minutes, and performing these reactions in open vessel mode allowed for rapid scale up of the chemistry to multigram amounts without having to change the reaction conditions.

Group VI Complexes

Group VI tetracarbonyl phosphine and tertiary amines complexes can be synthesized in just minutes in the microwave at moderate temperature, atmospheric pressure, and utilizing $NaBH_4$ as a catalyst.[2] These reactions were performed in alcohol solvents with borohydride salts which results in rapid heating of the reaction mixture under microwave irradiation. Several Group VI complexes were synthesized at reflux in the microwave with a reaction time ranging from 5 to 20 minutes. The reaction temperature was easily controlled by modifying the alcohol used as the solvent. This method also resulted in selective formation of the carbonyl complex in some cases. Pure cis-$(CO)_4(PPh_3)_2Mo$ was isolated in 73% yield in only 20 minutes at 85 °C, while higher temperatures or longer reaction times with conventional heating resulted in the trans isomer or a mixture of the cis and trans isomers. The microwave preparation of these common Group VI complexes features lower temperatures, shorter reaction times, benign solvents, and lower pressures as compared to the traditional thermal syntheses, thus providing a rapid, eco-friendly, and safe method that eliminates any concerns about high pressure.



Scheme 2.

Discover SP

Nanoparticles

Rh, Pd, and Pt nanoparticles can be prepared using a one-pot synthetic method that combines nucleation and growth using microwave irradiation.[3] It is known that having control over the addition rate of nanoparticle precursors gives improved experimental reproducibility, and being able to change the rate of the addition of the precursor can give control over the kinetics of particle growth. The open vessel feature of the CEM microwave systems allows for the incorporation of a syringe pump that can be used to very accurately control the rate of precursor addition. In this experiment the $RhCl_3$ precursor was added in an initial aliquot affecting nucleation of small isotropic Rh seeds (Figure 1). These seeds were then stirred isothermally for a period of time followed by the slow addition of a second aliquot of $RhCl_3$ and a second isothermal ripening. The slow addition allowed for the controlled growth of the resulting Rh nanoparticles. The nanoparticles prepared by microwave irradiation had several benefits over conventionally prepared materials, including improved monodispersity, morphological control, and higher crystallinity. The Rh nanoparticles also show higher catalytic activity compared to comparably sized conventionally prepared nanoparticles.

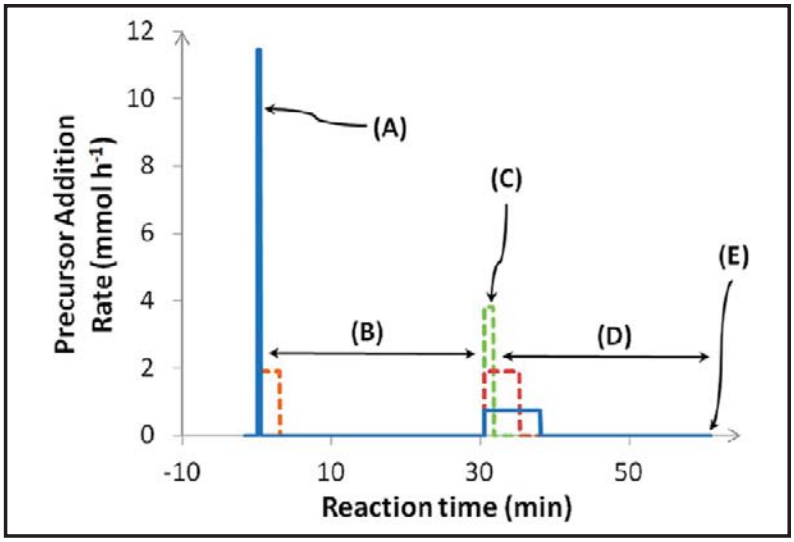


Figure 1. Syringe pump precursor addition rate programs employed to achieve controlled nucleation and growth: optimized conditions (blue) and examples of alternatives also studied (dashed lines); (A) nucleation phase; (B) seed ripening; (C) nanoparticle overgrowth; (D) nanoparticle ripening; (E) reaction quenched at 0 °C. (Reprinted with permission from reference 3. Copyright 2012 American Chemical Society.)

Conclusion

In each of three chemistries described above the open vessel feature of CEM microwave synthesizers was used to improve the synthesis results. The *N*-aryl hydrazones were prepared in high yields with short five minute reaction times giving multigram quantities in a single reaction. The Group VI carbonyl complexes were synthesized in less than 30 minutes with a safer and more environmentally friendly method. Lastly, the Rh nanoparticles were generated with a high degree of control by using syringe pump addition to control the rate of precursor addition.

References

1. La Regina, G.; Gatti, V.; Piscitelli, F.; Silvestri, R. *ACS Comb. Sci.* **2011**, *13*, 2-6.
2. Birdwhistell, K. R.; Schulz, B. E.; Dizon, P. M. *Inorg. Chem. Comm.* **2012**, *26*, 69-71.
3. Dahal, N.;García, S.; Zhou, J.; Humphrey, S. M. *ACS Nano* **2012**, *6*, 9433-9446.

APPLICATION NOTES

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