

Synthetic reactions using metal powders under microwave irradiation

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Liquid-phase synthetic reactions that require the use of metal powders are widely regarded as being unsuited to heating with microwave radiation, as they tend to exhibit destructive arcing. In a previous paper, we examined the factors that lead to arcing in these systems and, hence, how it may be controlled. This paper describes the application of those findings in a range of microwave-induced syntheses of organometallic and organic compounds, where metal powders are necessary. Although reaction yields were similar to those observed when conventional heating is used, the rapid nature of microwave heating leads to a slight reduction in reaction times.

Introduction

Microwave heating is an increasingly common tool in chemical synthesis, and the advantages and convenience of microwave dielectric heating are well documented.^{1,2} As a preparative method, the direct and rapid nature of microwave heating provides an efficient and rapid approach to a wide range of syntheses. Reports involving liquid reaction media are particularly interesting in view of the reported improvements in yields and reaction rates, and nowhere less so than in homogeneous organic reactions,^{3,4} where superheating effects are primarily believed to be responsible.^{5,6} Microwaves are now used routinely in analytical chemistry,⁷ liquid-phase organic and inorganic syntheses,² solid-state reactions,⁸ organic dry-media reactions,⁹ intercalation reactions¹⁰ and a wide range of other synthetic schemes. In spite of the range of applications and advantages of this heating method, reactions involving metal powders have not received great attention.^{11–14} We have previously reported on the advantages of microwave heating in solid-state reactions,^{11,13} whilst a number of authors also report enhanced reactivities in heterogeneous systems involving organic reactions on mineral supports. In the only previous report of microwave-induced synthesis using metals in liquid media¹⁵ the precursor materials form a slurry, in contrast to the well-dispersed metal powder–solvent systems described herein.

The neglect of this area may be related to the perception that the use of metal powders under microwave conditions invariably results in electrical arcing, which causes chemical decomposition. In high temperature solid-state reactions, where conditions tend to generate the most thermodynamically stable phases available to the system, the high energies of the electrical arcs do not present a problem.^{11–13} Reactions at low temperatures (typically those in the liquid phase), by contrast, are designed to generate products that are far from the thermodynamic minimum of the system and which are separated from the reactants or other products by relatively small energy barriers. The effect of high-energy arcing under these conditions therefore presents a serious problem. The effect is particularly pronounced with heterogeneous metal–liquid systems where it is not only visually dramatic, but may also be extremely destructive. Aromatic solvents, for example, invariably decom-

pose to yield carbonaceous material with even slight amounts of arcing.

The dominant problem for microwave-induced syntheses in metal–organic solvent systems is the selection of reaction conditions that exhibit the minimum degree of arcing. In this paper, we describe how synthetic reactions, requiring the use of metal powders, may be carried out in organic solvents safely and effectively.

In a previous paper,¹⁶ we reported the results of an extensive study into the phenomena which cause arcing to occur for metal powders in organic solvents. We proposed both a mechanism for arcing in heterogeneous metal powder–solvent systems and methods for reducing arcing to an acceptable level. We concluded that, although some of the factors are largely outside the reasonable control of the experimentalist (metal surface characteristics, for example), a large number of experimental factors may be varied so as to reduce arcing to an acceptable level. In particular, the use of low microwave power; polar solvents; high viscosity and high boiling points (or the use of higher pressures to increase solvent boiling point) all reduce arcing. We also noted that efficient stirring of a very fine metal powder reduces the amount of arcing, relative to that observed with poorly agitated coarse metal powders.

In addition to these factors, the level of arcing is highly dependent upon the number of metal particles per unit volume. Due to a number of conflicting phenomena, the severity of the arcing rapidly increases to a maximum level and then gradually decreases as the number of metal particles per unit volume increases. Fortunately, for the majority of reactions in which metal powders are employed, it is not necessary to use stoichiometric amounts of the metal, and the metal may be added either in excess at the start of the reaction or piecemeal as the reaction progresses. In this way, it is possible to optimise the metal particle concentration so as to minimise the level of arcing. Even where stoichiometric quantities of metal are required in a reaction, the most significant factor – the number of metal particles per unit volume – may be controlled either by appropriate selection of the metal particle size, or by varying the volume of the solvent. In our experience it is almost always possible to generate a set of synthetically acceptable experimental conditions under which arcing does not occur.

Apparatus

With the exception of syntheses at elevated pressures, the sample arrangement was the same in all cases. Microwave radiation (2.45 GHz) was applied using a multimode domestic microwave oven (Sharp R5V11B), which had been previously modified in-house to give continuously variable power (0 to 600 W).¹⁷ The base of the oven had also been modified to enable the use of magnetic stirrer fleas within the microwave cavity. Temperatures were monitored using a calibrated gas pressure thermometer¹⁸ or a fluoro-optic thermometer. The generic sample arrangement is shown in Fig. 1. The incident power was

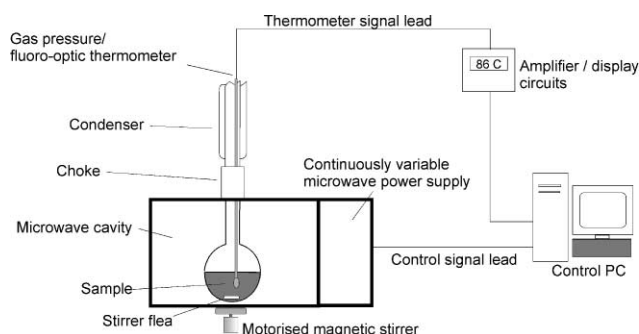


Fig. 1 Sample arrangement for microwave heating of stirred suspensions of metal powders in solvents.

manually controlled using a variable ac resistance. In all cases, the maximum power, which did not give rise to significant levels of arcing, was applied. In this way, the time required to reach the desired temperature was reduced in all cases to between 1 and 3 minutes. As soon as the required temperature was achieved, the power was reduced to a level that either held the temperature steady, or produced an acceptable level of reflux, as appropriate.

The specific conditions for each of the reactions are described in the Experimental section of this paper and the results of the syntheses are summarised in Table 1. The method was used in the synthesis of organometallic compounds and for organic transformations requiring metal powders.

Discussion

A number of reactions were chosen from the literature to give a representative range of reactions involving metal powders in organic solvents. Two synthetic routes to the well-known sandwich organometallic compound $[\text{Cr}(\text{C}_6\text{H}_5\text{CH}_3)_2]^+(\text{BPh}_4)^-$ were attempted. As the only reaction component that contributes to the dielectric loss tangent is the metal powder, these represent unusual reactions from a microwave heating perspective. In such cases, the susceptibility to arcing is raised considerably, and other means must be employed to reduce this possibility. This was achieved by using a relatively low number of metal particles per unit volume. Arcing was observed to a minor extent in both reactions, but by selecting a solvent such as toluene, with a relatively high boiling point, arcing was held at a level that was not detrimental to the synthesis. As anticipated, the chemical nature of the metal powder showed no significant influence upon the microwave heating properties of the reaction.

Although the benzene analogue of this material, $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+(\text{BPh}_4)^-$ could be generated under similar conditions to that of $[\text{Cr}(\text{C}_6\text{H}_5\text{CH}_3)_2]^+(\text{BPh}_4)^-$, the level of arcing was unacceptably high. Our previous paper demonstrated that the use of higher pressures would suppress arcing, by suppression of microscopic bubble nucleation on the metal particles. The synthesis of $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+(\text{BPh}_4)^-$ was therefore achieved through the use of a high pressure microwave reaction vessel.¹⁹ Namely, by raising the vessel pressure to an absolute value of

3 bar, using nitrogen gas, the boiling point of the benzene was raised to approximately 120 °C, thus suppressing arcing to acceptable levels, as determined by our previous studies.

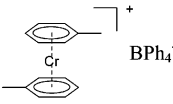
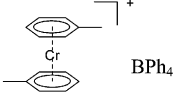
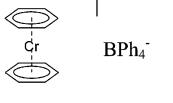
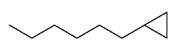
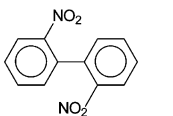
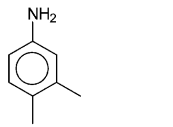
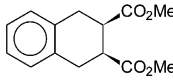
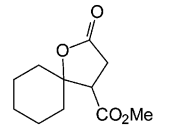
The syntheses of *n*-hexylcyclopropane, the γ -butyrolactone derivative, and 3,4-dimethylaniline further illustrate a conclusion of our previous paper. By including reaction components with significant dielectric loss tangents at microwave frequencies, there is sufficient attenuation of the microwave power that arcing is again reduced to acceptable levels. In these cases, diiodomethane, acetonitrile and nitrobenzene, respectively, are all known to be lossy (*i.e.* have a high dielectric loss tangent) at the frequency of the radiation (2.45 GHz). Whilst, in each case, the presence of these materials is a requirement for the reaction to take place at all, they have the added advantage of reducing arcing between metal particles under microwave irradiation. The same argument holds for the synthesis of 2,2'-dinitrobiphenyl *via* the Ullmann reaction, where the *o*-iodonitrobenzene simultaneously acts both to attenuate the microwave field strength, and allow direct heating of the reaction medium. This reaction uses the ability of copper to couple the aromatic rings. The metal morphology also effectively prevents arcing in this system. The copper powder that was used for this reaction consisted of extremely thin particles, each with a maximum thickness of the order of a few microns (measured using a scanning electron microscope). For copper at 2.45 GHz, the skin depth (*i.e.* the depth at which the incident microwave field is reduced to 1/e of its value at the surface) is of the order of 1.3 μm . Consequently, a significant fraction of the microwave power that is incident upon the particles passes through the metal, and the heating which results may be considered volumetric, and not simply a surface phenomenon. Two other factors are also important. Firstly, the high surface area of the particles also increases the rate at which heat can be lost to the solvent, and the efficient cooling of the metal surface reduces the effectiveness of bubble formation. Secondly, the number of suitable nucleation sites that would be available in such thin metal particles is extremely small; a factor that our previous study concluded would reduce the probability of arcing taking place. It was possible, therefore, to perform this reaction without any significant arcing being observed. Indeed, this metal powder was so resistant to arcing that a suspension in benzene, a solvent that is normally destroyed by arcing in the presence of metal powders, could be efficiently heated using microwaves without any visible arcing taking place.

The zinc promoted coupling of *o,o'*-dibromo-*o*-xylene and maleic acid dimethyl ester does not give any measurable yield of product with conventional heating, although a reported yield of 89% has been reported when the reaction is undertaken using ultrasound. Our objective in attempting this reaction was to determine whether microwave heating could be efficiently localised on the metal particles, so that the activity of the metal could be raised above that obtained through conventional, thermally equilibrated, heating. Under microwave irradiation, however, no evidence of a reaction could be detected even after 10 hours of reflux. This indicates that, although the microwave heating effect is localised on the metal particles, it cannot emulate the effect of ultrasound activation, which acts by continuously exposing 'clean' metal surfaces to the reactants.

Conclusion

Despite the widespread observation that metal powders, when exposed to high power microwave fields, are hazardous and destructive, we have demonstrated that synthetic reactions involving metal powders may be successfully performed in volatile and inflammable solvents using microwaves. In our view, arcing is reduced significantly in solvents or reaction components that have relatively high dielectric loss tangents. There is therefore no reason why these reactions may not be performed using microwave heating techniques. Furthermore,

Table 1 Reactions involving metal powder suspensions in solvents under microwave irradiation

Reactants	Product	Time	Yield (conventional)	Ref.
Cr + toluene + AlCl ₃ + HCl		20 minutes	52% (51%)	20
Al + toluene + AlCl ₃ + CrCl ₃		30 minutes	49% (53%)	21
Al + benzene + AlCl ₃ + CrCl ₃		30 minutes	45%	21
Cu/Zn + CH ₂ I ₂ + oct-1-ene + I ₂		15 hours	52% (70%)	22
Cu + <i>o</i> -iodonitrobenzene		1.5 hours	65% (61%)	23
Sn + HCl + 4-nitro- <i>o</i> -xylene		50 minutes	94% (97%)	24
Zn + α,α' -dibromo- <i>o</i> -xylene + maleic acid dimethyl ester		10 hours	0% (89%, ultrasound)	25
Zn + 2-iodopropane + acetone + maleic acid dimethyl ester		0.5 + 3 hours	64% (86%)	26

where low dielectric loss solutions cannot be avoided, suitable choice of reaction conditions (*e.g.* high pressures, or reduced number of metal particles per unit volume) or suitable choice of metal powder morphology (preferably submicron particles or thin leaves) may reduce the level of arcing. Even in the most extreme cases, these techniques may be used to reduce the degree of arcing to acceptably low levels. More often, conditions may be developed where arcing may be eliminated completely.

Superficially, the use of microwave heating does not offer any appreciable advantages over conventional heating. The reactions studied in Table 1 have demonstrated that microwaves may be used to complete reactions involving metal powders. The reactions were not chosen to demonstrate any significant reaction rate enhancement or improved reaction yields, for such procedures. Further work will be required to establish this. It should be borne in mind that the reaction times in this paper have been calculated from the start of the reflux process. Because microwave heating is direct and reduces the need to heat, for example using heating mantles or oil baths, reflux conditions are achieved rapidly, so reducing the overall reaction time by as much as 25% when compared to conventional heating.

Experimental

In all cases, metal powders were used directly as obtained from the supplier. No attempts were made to remove oxide coatings, or otherwise to modify the properties of the powders.

Synthesis of [Cr(η -C₆H₅CH₃)₂]⁺(BPh₄)⁻

Method 1.²⁰ AlCl₃ (5.2 g) and chromium powder (Aldrich, 99.5%, -100 mesh, 1.0 g) were ground together and placed in a 250 cm³ round-bottom flask. Stills-dried toluene (150 cm³) was saturated with HCl gas, and added to the flask and the reactants heated at full power (600 W) for 20 minutes. Degassed deionised water was added to the cooled reaction mixture and the green aqueous layer isolated. A solution of Na(BPh₄) was added, and the resulting precipitate separated by filtration, washed with deionised water, and dried overnight in a vacuum desiccator. Yield: 52% (literature yield using conventional heating: 51%). Analysis: C 82.7%, H 6.1% (Calculated for C₃₈H₃₆BCr: C 82.2%, H 6.5%).

Method 2.²¹ AlCl₃ (12.0 g), CrCl₃ (5.0 g), and Al powder (Alpoco, 99.5%, -100 mesh, 0.7 g) were ground together and added to 200 cm³ of stills-dried toluene. The reactants were heated to reflux using 600 W microwave power for 30 minutes and the resulting solution worked up as for method 1. Yield: 49% (conventional heating: 53%). Analysis: C 82.4%, H 6.2% (Calculated for C₃₈H₃₆BCr: C 82.2%, H 6.5%).

Synthesis of [Cr(η -C₆H₆)₂]⁺(BPh₄)⁻²¹

AlCl₃ (12.0 g), CrCl₃ (5.0 g), and -100 mesh Al powder (Alpoco, 99.5%, -100 mesh, 0.7 g) were ground together and added to 200 cm³ of stills-dried benzene. The reactants were

sealed in a microwave pressure vessel and an overpressure of dry, oxygen-free, nitrogen (1 bar) introduced. The reagents were stirred using a magnetic stirrer and heated, using 100 W microwave power, to generate a pressure of 2 bar. This pressure was maintained for 45 minutes and the resulting solution worked up as for $[\text{Cr}(\eta\text{-C}_6\text{H}_5\text{CH}_3)_2]^+(\text{BPh}_4)^-$. Yield: 45 % (conventional heating: 51%). Analysis: C 82.3%, H 6.2% (Calculated for $\text{C}_{36}\text{H}_{32}\text{BCr}$: C 82.0%, H 6.1%).

Synthesis of n-hexylcyclopropane²²

This reaction was performed using the literature procedures and was based on the following quantities. Oct-1-ene (4.15 g), diiodomethane (5.09 g), iodine (0.51 g). Although several methods of preparing a zinc-copper couple were attempted, the best results were obtained using a commercially available material (Aldrich, laboratory grade reagent, 3 g). Heating was effected using 80–100 W applied microwave irradiation for 15 hours. Products were separated by distillation under reduced pressure. Yield: 52% (conventional heating: 70%). The product was characterised using IR and NMR spectroscopy. IR cyclopropane peaks at 1014, 3001, and 3070 cm^{-1} . ^1H NMR (CCl_4 , 200 MHz): δ 0.10–0.80 (m, 5H, cyclopropyl), 0.85–1.75 (m, 13H).

Synthesis of 2,2'-dinitrophenyl (Ullmann reaction)²³

This was prepared broadly using the method described by Fuson and Cleveland.²³ *o*-Iodonitrobenzene (10 g) was melted under microwave irradiation (80 W) with stirring, and copper powder (Aldrich, 99.5%, –325 mesh, 5 g) added over a period of approximately 20 minutes to reduce the amount of arcing. The temperature, monitored with a gas pressure thermometer, was maintained at between 215 and 225 °C for 1.5 hours. The products were worked up as described in the literature. Yield: 65% (conventional heating: 61%). Analysis: C 59.2%, N 11.5%, H 3.3% (Calculated for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4$: C 59.0%, N 11.5%, H 3.3%). mp 122–124 °C (literature²³ 123.5–124.5 °C).

Synthesis of 3,4-dimethylaniline²⁴

4-Nitro-*o*-xylene (9.0 g) and tin powder (Aldrich, 99.5%, –100 mesh, 11.25 g) were placed in a reflux apparatus in the microwave oven, and 25 cm^3 of concentrated hydrochloric acid slowly added. Once the vigorous heating had subsided, the reactants were heated under microwave irradiation (approximately 40 W) for 60 minutes. The product was then purified using the procedure described in the literature.²⁴ Yield: 94% (conventional heating: 97%). Analysis: C 78.4%, N 11.7%, H 9.7% (Calculated for $\text{C}_8\text{H}_{11}\text{N}$: C 79.3%, N 11.6%, H 9.1%).

Zinc promoted synthesis of a γ -butyrolactone derivative²⁵

Under a nitrogen atmosphere, zinc powder (Alfa, –200 mesh, 4.8 g) was stirred in a solution of 2-iodopropane (4.4 cm^3) in

acetonitrile. This was refluxed using microwave irradiation (40 W) for 30 minutes. Dimethyl maleate (2.30 g) and acetone (2.4 cm^3) were dissolved in acetonitrile (10 cm^3) and slowly added over a period of 30 minutes. The reactants were heated for a further 3 hours using microwave irradiation (40 W) before being worked up by the method described in the literature.²⁵ Yield: 2.25 g (64%, based on dimethyl maleate). Analysis: C 81.9%, H 6.7% (Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C 82.2%, H 6.5%).

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