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Arcing and other microwave characteristics of metal powders in liquid systems

A. Gavin Whittaker[a] **and D. Michael P. Mingos**[b]

[a] *University of Edinburgh, Department of Chemistry, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: g.whittaker@ed.ac.uk*
[b] *St. Edmund Hall, University of Oxford, Oxford, UK OX1 4AR. E-mail: michael.mingos@st-edmund-hall.oxford.ac.uk*

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The factors which cause arcing in metal powder–solvent systems under microwave irradiation have been systematically investigated. A mechanism which fully accounts for the observations is proposed together with guidelines for the minimization or prevention of arcing under such conditions. The studies presented herein will enable synthetic reactions to be performed under these conditions.

Introduction

The phenomenon of microwave dielectric heating in synthetic chemistry is well documented,[1,2] with the use of microwave heating devices becoming increasingly common in the laboratory. The rapid, direct nature of microwave heating manifests itself in the form of decreased reaction times and increased yields. Reports involving liquid reaction media are of particular interest, nowhere more so than in homogeneous organic reactions,[3–5] where superheating effects are believed to be primarily responsible for the improved yields and rates of reaction.[6–9]

Microwave heating has been employed in an ever-expanding range of syntheses in the last decade. However, although a number of authors have reported enhanced reactivities in microwave-heated supported metal catalysts,[10–13] to the best of our knowledge, there has been only one report of metal powders being used in conjunction with liquid media for synthetic purposes.[14] Even here, the density of metal powder used was such that the reactants were in the form of a slurry, rather than the well dispersed metal powder–solvent systems described here.

The reasons for this lack of investigation may be the perception that the use of metal powders under microwave conditions invariably results in very destructive electrical arcing. The effect is pronounced with heterogeneous metal–liquid systems, where it is not only visually dramatic, but may also be extremely destructive and potentially hazardous. In this case, the arcing appears to be random in its behaviour and appearance, uncontrollable, dangerous, and destructive enough to decompose the reactants to carbonaceous material.

The dominant problem for microwave-induced syntheses in metal powder–organic solvent systems is the selection of reaction conditions which exhibit the minimum degree of arcing. In an ideal reaction scheme, no arcing would be observed, although this may be extremely difficult to achieve, particularly, as we discuss later, in the case of aromatic solvents.

This paper reports on an improved understanding of the factors which affect arcing in metal–liquid systems and how it may be controlled by judicious choice of experimental parameters. We look initially at the heating characteristics of these systems before describing a systematic investigation into arcing in metal powder–solvent mixtures. By observing the level of arcing as a function of solvent, metal concentration and applied microwave power, we have begun to understand the factors which affect arcing and how it may be controlled. In a subsequent paper, we will describe how, under microwave irradiation, chemical syntheses are possible in these heterogeneous systems. The use of metal powders under controlled microwave conditions also has implications for matrix isolation and metal vapour synthesis applications.

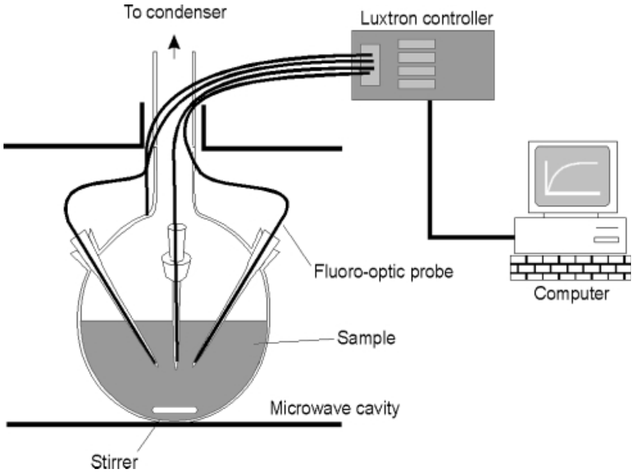

Fig. 1 Arrangement for measurement of power absorbance in liquids.

Experimental details

Power absorbance characteristics of metal powder–solvent systems

A round-bottomed flask fitted with four glass probe holders was placed with a condenser in the microwave oven (Fig. 1). A fluoroptic probe, run through a port in the cavity roof, was placed into each probe holder. The temperature recorded by each probe was fed to the Luxtron data logging controller. The data from the controller were then fed, in real time, to an IBM PC-XT computer and recorded using the Labtech Notebook software for data acquisition, Labtech, Andover, MA. A fixed power domestic microwave oven (Swan, 500 W) was used. Temperature variation between the four probes was generally less than 0.5 K, due to the rapid stirring, and reported temperatures are the mean of the four values at the specified time.

Various masses of copper powder were dispersed by stirring at constant speed in 100 cm^3 of dry hexane, with both solvent

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and metal being replaced for each measurement. A practical upper limit on the metal mass of 18 g was encountered, as larger quantities could not be completely retained in suspension and probe damage through arcing then became a danger.

Arcing studies

The physical properties of the metal powder used in microwave work have been found to have a large effect on the degree of arcing which is observed. Systematic investigations into the effect of metal particles on arcing could not be easily carried out, since there are a large number of ill-defined variables in commercially available metal powders. Morphology, particle size, and metal composition, for example, all appear to influence the arcing process. For this work, a single batch of −100 mesh aluminium powder (The Aluminium Powder Company, Sutton Coldfield, UK) was used in order to eliminate any metal-dependent effects. The powder was used as supplied and no attempt was made to clean or otherwise modify the metal. The investigations were carried out in a range of solvents in a multimode oven (Sharp R5V11, 600 W) modified to deliver variable power. The degree of arcing which is displayed in any system is difficult to quantify, but for the purposes of this work, six arbitrary categories were created, based on previous experience:

0—No arcing observed.
1—1–5 sparks min^{-1}.
2—6–60 sparks min^{-1}.
3—60+ sparks min^{-1}, no solvent decomposition observed.
4—Violent arcing which eventually decomposes solvent.
5—Violent arcing which yields visible amounts of carbon in under 10 s.

The metal mass and microwave power dependencies were investigated and, for each metal–solvent system, the extent of the arcing was evaluated according to the scheme above. The time taken for the analyses was limited in each case, so as to prevent any changes in the metal morphology, with the metal powder and solvent being completely replaced at regular intervals.

Power absorbance characteristics of metal powder–solvent systems

Preliminary experiments readily demonstrated that no solvent superheating effect is observed. Superficially, this contrasts with the findings of a number of authors, who have found that solvents may heat to some tens of degrees above their conventional boiling points under microwave irradiation.[6,7] The reasons for the absence of superheating are readily apparent however, since it has been proposed that boiling point elevation in microwave heating arises from the absence of bubble nucleation sites in the solvent body.[7] The presence of literally millions of nucleation sites on the metal powder particles does not allow any substantial volume of the liquid to become superheated before boiling commences from the metal surface. In the particular case of metal powders suspended in an apolar solvent, the heating does not actually originate in the liquid, but arises from conductive heating in the metal powder, and in these cases boiling will arise from the direct heating of nucleation sites in the metal particles.

The initial heating rate was determined from the measurements of temperature against time. The heat capacity for each system was calculated and used to calculate the initial power absorbance. The resulting relationship between the power absorbed and the mass of metal is shown in Fig. 2.

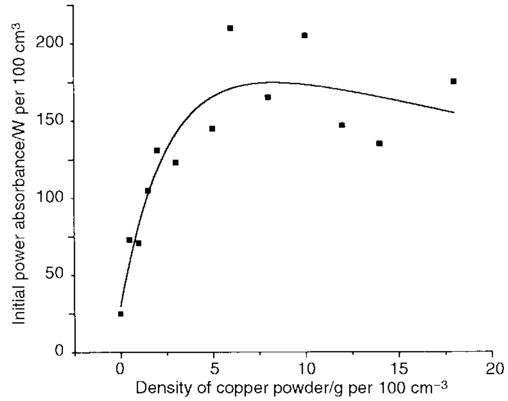

Fig. 2 Power absorbance as a function of copper density in hexane (200 cm^3, 600 W irradiation).

At low metal loading, the power absorbed increases with increasing copper density in a broadly linear fashion. As the density of metal is increased in the sample, the proportion of incident microwave power increases correspondingly. With increasing metal loading, the gradient gradually decreases, and the curve passes through a distinct maximum at between 6 and 8 g of copper, before slowly decreasing. For the reasons given previously, the reliability of the measurements decreases at higher metal densities, but generally indicate a decrease in the heating rate with increasing metal density. This is not unexpected, since the system becomes increasingly conducting with higher copper density, and reflection of the incident power becomes the dominant characteristic. At the limiting density of 8960 g dm^{-3} (representing a solid block of copper) over 99.9% of the incident power is reflected.

The heating rate is only poorly reproducible and decreases slowly when a copper density of >180 g dm^{-3} is used in hexane. This leveling may be attributed, in part, to insufficient agitation of the additional metal powder. Since there exists a limiting quantity of metal which may practically be suspended in the sample, any powder in excess of this amount tends to be little disturbed by the stirrer bar, and contributes little to the heating process.

The maximum absorbed power is approximately 200 W, which represents only 33% of the total power delivered by the microwave oven. The same volume and geometry of water, by comparison, absorbs approximately 90% of the available power. The decrease in the absorbed power is attributed to the increased reflectivity of the hexane–copper mixture. As the density of copper powder is increased, the proportion of the microwave power which penetrates into the sample is diminished, the reflected proportion being dissipated as heat in the magnetron and oven walls.

Arcing in metal powder–solvent systems

Preliminary qualitative studies indicated that numerous factors affect arcing in metal–solvent systems. Arcing is observed as randomly distributed electrical discharges in the outer few centimetres of the metal–solvent system under microwave irradiation. Little or no arcing is observed in the core of the sample, an effect which may be attributed to attenuation of the electric field by the metal particles. It may be localised in some circumstances, particularly at the base of the sample where poorly dispersed particles accumulate, suggesting that the proximity of metal particles has a significant bearing on the arcing mechanism.

Arcing is not uniform in time. Once arcing has occurred, the metal may become altered in the process making it more susceptible to arcing under subsequent irradiation. In a typical example, 0.5 g of aluminium powder (−100 mesh) suspended by stirring in 200 cm^3 of toluene required 600 W irradiation to initiate arcing. After 20 s of 600 W irradiation and a 10 min pause for cooling, arcing could be restarted with as little as 200–300 W irradiation. Carbon formation effects were discounted by decanting the toluene, washing the aluminium with clean toluene, and repeating the experiment. Ultrasound treatment of the aluminium–toluene mixture restored the original properties

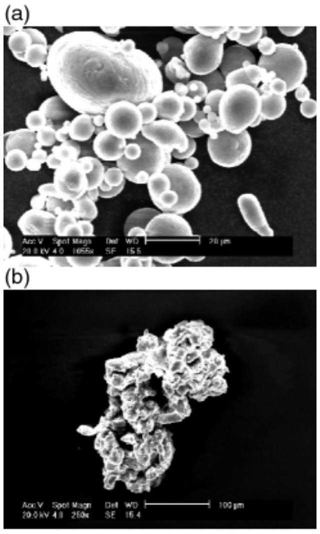

Fig. 3 Metal particles before (a) and after (b) arcing in an inert non-polar solvent.

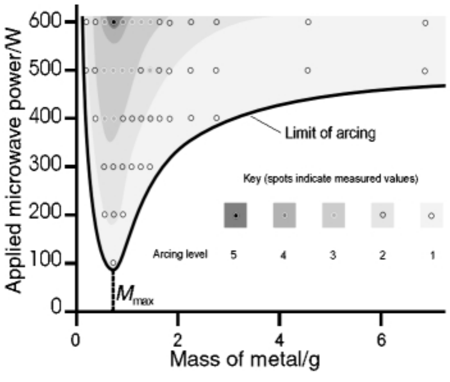

Fig. 4 Typical arcing profile (toluene).

of the system and Scanning Electron Microscopy (SEM) revealed that the aluminium particles become loosely welded to one another in a manner which evidently contributes to the arcing properties (Fig. 3). It appears that as larger particles of this type are formed they are more susceptible to arcing, an observation which is in keeping with the higher electric field gradients which may be induced on them. The formation of these aggregates supports the conjecture that arcing occurs *between* metal particles.

Arcing in unsaturated solvents, in particular, is a relatively short-lived but violent phenomenon and requires frequent replacement of both metal and solvent. The carbon formed in the breakdown of aromatic solvents may come to dominate the microwave heating effect, even though the quantities responsible are remarkably small (*ca.* 100 mg dm^{-3}). It may be noted in passing that no spectroscopic evidence (UV–Vis, IR, NMR) for the formation of fullerenes was observed in any of the metal–solvent arcing systems which we studied.

Using results from the 'quantitative' observations, an arcing profile could be mapped out for each solvent which represented the degree of arcing as a function of the mass of aluminium and the applied power (see Fig. 4). Approximate contours for the extent of arcing could be laid over the measurements, and in each instance had an identical form. It is highly significant that a number of polar solvents, including water, primary alcohols of general formula $CH_3(CH_2)_nOH$ ($n = 0$, 1, 2, 3), and the tertiary alcohol $(CH_3)_3COH$ were not observed to support arcing. These solvents are therefore very attractive for synthetic procedures involving metal powders.

Interpretation of the arcing profiles

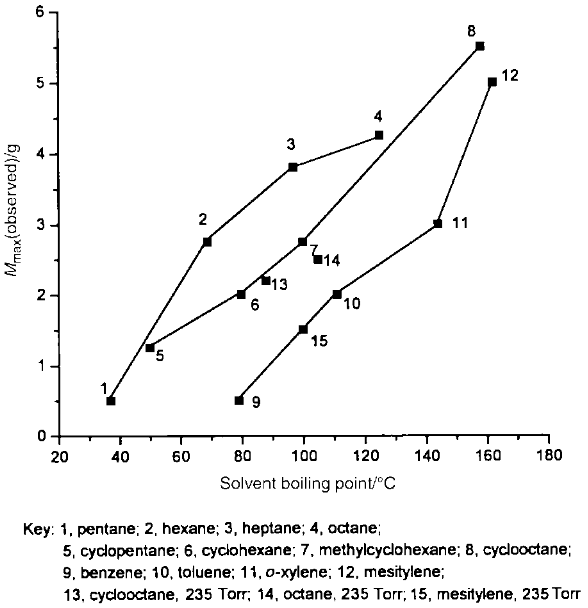

Fig. 5 M_{max} plotted as a function of solvent boiling point.

Two important features are common to all of the profiles. Firstly, there is an obvious increase in the degree of arcing as the power is increased. The electric field strength is directly related to the square root of the microwave power and, as expected, the electric field strength appears to influence the rate at which electric discharges occur. A second feature is that whilst there is a propensity for arcing to increase with the metal loading, as might be expected, there is a cusp in this curve beyond which increased metal loading decreases the susceptibility for arcing. This correlates with the observations of the effect of metal loading upon the heating rate discussed previously. As the density of suspended metal particles increases, the penetration depth of the microwaves decreases, and the effects of reflection become important in decreasing the electric field strength in the sample body. Other observations, however, suggest that there are some minor complications to this model. Firstly, the cusp is much less pronounced when larger metal particles are excluded from the system by sieving. This is in contrast to the profile seen for −40 mesh aluminium powder in toluene, for which the position of the minimum is decreased relative to that of −100 mesh aluminium. This suggests that the largest particles in the suspension are mainly responsible for the arcing which is observed, and that smaller metal particles, which are more easily suspended, act as more efficient microwave susceptors and reflectors.

The minimum quantity of metal required for arcing to occur is heavily solvent dependent, varying from 0.5 g for cyclopentane through to approximately 12 g for carbon tetrachloride. There proved to be no single parameter with which to formulate a relationship between arcing and the physical properties of the solvent. However, a plot of the mass of aluminium required to give the maximum degree of arcing (M_{max} on Fig. 4) against the boiling point of the solvent is shown in Fig. 5, and displays some interesting features. A graph of this type gives reasonably straight line plots for the three types of organic solvent used—straight chain alkanes, cycloalkanes, and methylbenzenes. It is readily apparent from this graph that there is a direct relationship between the boiling point of the solvent and the maximum in the arcing. Higher boiling point solvents in a given series of similar compounds require a larger amount of metal powder in order for arcing to occur. The correlation was verified by decreasing the boiling point of several solvents under reduced pressure. The boiling point of the solvent at the lower pressure was obtained from a nomograph,[15] and measurements taken of the extent of the arcing in the same way as at atmospheric pressure. The results of this work show a very clear decrease in the amount of metal required to cause

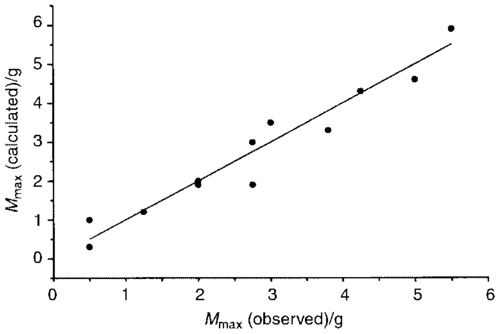

Fig. 6 Correlation of calculated M_{max} with observed values.

arcing as the pressure is lowered. The properties of the solvents run at low pressure remain approximately in line with the other members of the same chemical family on the graph.

It is clear from the plot shown in Fig. 5 that less metal is required to initiate arcing in aromatic solvents than in alkyl solvents with similar boiling points. A number of differences in the physical properties of these two types of compound may be invoked to explain this. However, the boiling point dependency suggests that at some stage in the arcing process the solvent is vaporised and, given the relatively high field strength in such vapour bubbles, it seems reasonable to conclude that the discharge is occurring, at least in part, through the solvent vapour. The factors which affect the electrical breakdown and generation of high voltage sparks in gaseous media are well known, major contributors being the ionisation potential and the collision cross section of the molecule with free electrons.[16] It appears that the ionisation potential of the molecules may in itself explain the differences between the different chemical families. There is a clear increase in the quantity of metal required to obtain the minimum in the arcing profile as the ionisation potential of the solvent increases, and the following relationship was found to hold extremely well for the system studied (Fig. 6):

$$M_{max}\,(\mathrm{g}) = [(0.064 \times B) + (1.82 \times I) - 3.6]$$

where B and I are the solvent boiling point (K) and ionisation potential (eV), respectively, and M_{max} is as previously defined. Note that the numerical values of the constant terms in this relationship are specific to this particular combination of metal powder and apparatus. Variations in such parameters as the microwave field geometry or the nature of the metal may have a profound effect on the characteristics of the system.

Any proposed arcing mechanism must account for the fact that, although there is a dependency upon the boiling point, solvents do not need to be boiling in order for arcing to occur. Indeed, arcing appears to be most dramatic *below* the boiling point and may actually diminish markedly as boiling commences, suggesting that vaporisation of the solvent is occurring at a microscopic rather than at the macroscopic level. This may be interpreted in the light of conventional nucleate boiling theory.[17,18] In a metal under microwave irradiation, the heating process is predominantly a surface phenomenon. For example, in the case of aluminium which is exposed to a microwave field with a frequency of 2.45 GHz, approximately 90% of the unreflected incident power is dissipated in the uppermost 5 microns of the metal. Since it is within this surface layer that the cavities and nucleation sites exist, microwave irradiation of dispersed metal powders will result in those cavities, and the vapour which they contain, being heated. Some of the energy will also be dissipated to the fluid in contact with the metal surface, and the combination of these two effects allows the localised formation of vapour bubbles on the surface of the metal. Any bubbles released from the surface of the metal will rapidly collapse on passing into cooler volumes of the liquid. Macroscopic boiling need not occur for such microscopic bubbles to form.

Since electrical breakdown occurs much more readily in gases than in liquids, the bubble nucleation process allows the dependency of arcing on boiling point and ionisation potential to be explained by an extremely simple mechanism. As metal powder is added to a solvent, a bubble nucleation process will take place as the microwave radiation heats the surface of the metal powder particles. This process will be most efficient in solvents with low boiling points, and whilst high boiling point solvents may still form bubbles, these will collapse much more rapidly on contact with the relatively low temperature solvent. The lifetimes of these bubbles will be long enough to allow close contact with a second metal particle, and electrical discharge through the vapour. In this dynamic situation, the number of sites available for the particles to discharge through remains approximately fixed, but the rate at which discharging may occur is now limited by the frequency with which particles approach one another. As the quantity of metal in the system is increased, so the density of metal is increased, discharges between metal particles become more likely. However, the distance through which arcs may occur is also decreased, whilst the reflectance of the sample is increased and the electric field density decreased by attenuation of the field through heating from induced currents. Both of these effects will decrease the frequency of discharges. This possibility, together with the increased reflectivity of the sample, may explain the cusp in the power–mass plot. Clearly, higher microwave power also means that lower metal densities are required for a given amount of arcing, as the induced electrical potentials are also increased.

It should be noted that this interpretation is only valid for relatively low densities of metal powders in solvents. Where arcing is observed in a metal powder–solvent slurry, rapid heating of the sample, vaporises the solvent on a macroscopic scale, and discharges may occur through macroscopic volumes of vapour.

An important parameter is revealed by the anomalous behaviour of aluminium suspended in carbon tetrachloride. This combination displays a minimum in the arcing profile with approximately 12 g of aluminium. On the basis of the preceding information and extrapolation of the data on the graph, it should be expected that CCl_4, with a boiling point of 350 K and ionisation potential of 11.60 eV, would give a minimum with approximately 5–6 g of aluminium powder. In this instance, the density of the liquid becomes a dominant factor in the arcing process. With high-density solvents, effective dispersal of the metal through the solvent becomes easier to achieve. Consequently, more metal is required before the particle density at any point is sufficiently great to sustain arcing. In less dense fluids, the larger particles are less easily dispersed and, even with aggressive stirring, the particle densities maximise towards the base of the sample. This requires correspondingly less metal for arcing to occur.

The absence of arcing in polar solvents may be attributed to considerable attenuation of the microwave field strength by the high loss tangent of the solvent.

The factors which influence arcing

Our hypothesis allows the interpretation of the factors which either directly or indirectly affect arcing under the experimental conditions used in the course of this work. Moreover, it makes it possible to tailor conditions in a given reaction so as to reduce the amount of arcing which may take place. In order to make the discussion more economical, an arbitrary parameter denoted as A, the tendency for arcing, is used for convenience. An increase in A indicates an increase in the ability to create arcing at low metal concentrations. A second parameter, R, is used to denote the range of metal concentrations over which arcing occurs.

Metal morphology. The morphology of the metal has a profound effect on the extent of arcing, since it depends on the existence of nucleation sites. For metal particles with high densities of surface cavities, A will be much greater than those with few or no cavities. Since determination of the number of potentially suitable nucleation sites is not trivial, this factor, above all others, limits our ability to predict the extent of arcing with any degree of accuracy. In addition, the shape of individual particles will have a bearing on the process. Sharp points, for example, will concentrate charge, and if nucleation sites occur in these regions a higher value for A will occur than for spherical particles with otherwise identical physical characteristics.

Metal particle size. A number of factors are influenced by particle size. A given electric field strength will induce larger voltages across large particles than across smaller ones. This not only increases A in systems with large metal particles, but also gives an increase in R. The increase in induced voltages allows arcing at lower metal concentrations, but as the mass of metal is increased, fewer particles are added compared with addition of the same mass of smaller particles. Correspondingly, the factors which influence the value of R (reflectance, attenuation due to heating effects, proximity of particles, *etc.*) do not increase so rapidly with mass for larger particles. A secondary effect results from the ease with which particles of a given size may be dispersed in a solvent. This is dependent on the rate of stirring and solvent density and viscosity as discussed below, but it should be noted that larger particles are less easily dispersed than smaller ones.

Metal conductivity. In principle, for a given morphology and particle size, A is maximised for those metals whose skin depth is such that most of the energy is dissipated to a depth approximately equal to the size of bubble nucleation sites. This efficiency will depend on both the size of the nucleation sites, and the skin depth of the metal. The latter quantity depends upon the conductivity of the metal, and for those metals with a relatively small skin depth (Cu and Au, for example) poorer skin heating effects and higher reflection coefficients are to be expected. A consequent decrease in the efficiency with which bubble formation may occur is to be expected in these cases. At the other extreme, non-metallic conductors such as carbon, whose skin depths are rather larger than the depth of the bubble nucleation cavities, will display inefficient heating of those sites, together with rather lower induced potentials. In both of these cases, A is smaller than that in metals with skin depths which have the same order of magnitude as the size of the nucleation sites. In practice, however, it may well be virtually impossible to test this hypothesis, as preparing samples of different metals with comparable morphology and nucleation sites would be extremely difficult, and it seems likely that morphological differences may well be the dominant effect.

Solvent boiling point. As previously discussed, the boiling point of the solvent is directly proportional to the amount of metal required to both initiate and to maximise arcing in a system. A therefore increases with decreasing boiling point.

Solvent ionisation energy. A low ionisation energy for the solvent allows easier electrical breakdown of the vapour than for a solvent with a high ionisation energy. Consequently, in those solvents with low ionisation potentials, the metal particles do not require such close contact with each other in order for arcing to occur through the vapour (and possibly through the liquid, also). This increases the probability of arcing occurring at lower metal particle densities and correspondingly, A increases.

Solvent dielectric loss tangent. In solvents which have significant dielectric loss tangents, the electric field may be rapidly attenuated on passing through the metal–solvent system. The decrease in electric field strength decreases the induced voltages in the metal (and thus A) and in extreme cases (notably alcohols and water) arcing may not be observed at all. With higher applied powers than those used here it is likely that arcing would occur, although such power levels would be neither readily available, nor of practical benefit in synthetic studies.

Solvent viscosity and density. The effect of higher solvent viscosity and density is to increase the dispersion of the metal powder through the solvent. Up to a limiting point, A is expected to decrease with both increasing viscosity and increasing density.

Applied power. The applied power is directly related to the electric field strength. Decreasing the field strength decreases the amount of arcing which is observed. Power control is extremely important in liquid systems, since excessive microwave power may cause violent 'bump' boiling. When using metal powders in conjunction with organic solvents and, in particular, arenes it is essential to be able to vary the applied power, since arcing which will decompose the solvent may occur.

Rate of stirring. If the rate of stirring is very low, insufficient agitation may occur for the metal to be dispersed in the solvent body. In the extreme case, with no stirring, a metal–solvent slurry exists at the base of the sample. Both R and A are large in this case. R and A decrease with increased stirring until a limit at which all the metal powder is evenly dispersed throughout the solvent. Beyond this limit, all arcing effects are dependent upon factors other than the rate of stirring. It is particularly important when using metal powders that the reaction components are stirred in order to disperse the metal powder throughout the solvent.

Reaction pressure. Decreasing the pressure in the vessel decreases the boiling point of the solvent. A is increased, R appears to be little affected.

Conclusions

The application of microwave dielectric heating to reactions involving metal powders is counter-intuitive, yet it has been demonstrated that such synthetic procedures may be performed effectively and safely. This paper defines for the first time the important parameters associated with the phenomenon of arcing of metal powders in organic solvents. It may be appreciated from the data presented in Fig. 6 that we have been able to establish a very effective relationship between arcing and the nature of the solvent properties, and to propose a mechanism which accounts for our observations. In our model, arcing depends upon the ability of metal particles to locally heat the solvent and create a vapour pathway through which electrical discharges may pass. These results have practical implications for synthetic chemists who wish to study metal powder reactions; our applications of these techniques will be described in a subsequent paper. Although numerous factors affect arcing, most of these are outside the control of the experimentalist for all practical purposes. However, the synthetic chemist *does* have effective control of the following: choice of solvent, applied microwave power, density of metal, rate of stirring, pressure. This enables *most* syntheses involving metal powder–solvent systems to be accomplished with the assistance of microwave dielectric heating. Thus, in designing syntheses of this type, the following conditions are generally desirable if arcing is to be avoided: low microwave powers, high boiling point solvents and/or high pressures, non-aromatic solvents (preferably high loss polar solvents such as alcohols), and small, well-dispersed metal particles.

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