

Design and application of a reflux modification for the synthesis of organometallic compounds using microwave dielectric loss heating effects

David R. Baghurst and D. Michael P. Mingos

Abstract

A commercially available microwave oven has been modified so that syntheses involving the refluxing of organic solvents can be safely and conveniently undertaken. The applications of this technique for accelerating the rates of reactions leading to the synthesis of some commonly used organometallic and coordination compounds are described.

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The application of microwave dielectric loss heating effects for accelerating organic [1,2], organometallic [3,4] and solid state [5] reactions is now well documented. For solution reactions the most promising results have been obtained by use of sealed Teflon containers, which can sustain temperatures of 250 °C and pressures up to 80 atm. Whilst these containers provide a means of reducing the times of many syntheses by two or three orders of magnitude and preventing the escape of flammable solvents into the microwave cavity, which could cause an explosion if initiated by a spark, they do have several disadvantages. Firstly, the superheating effects arising from the high pressures generated in the container can lead to decomposition of the product [3]. Secondly, the very large acceleration of the reaction time and the high pressures generated can mean that it is difficult to control the reaction, especially when it is complete in less than a minute [3]. Finally, the Teflon containers are not cheap (ca. \$500) and their lifetimes can be short if the conditions used consistently approach the limits specified by the manufacturer.

In this communication we describe a modification of a microwave heating system which enables a chemist to heat solutions using microwave dielectric loss heating effects and reflux them safely. The conventional chemical reflux system cannot be introduced into a microwave cavity because the circulating water coolant would absorb microwaves very strongly and heat up very rapidly. An air condenser would not be effective in returning the flammable solvents safely to the reaction flask. One solution to the problem would be to use a coolant which does not absorb micro-

Table 1

Comparison of reaction times and yields using the modified reflux microwave apparatus compared with those for conventional and microwave-container methods

| Reactants | Product | Solvent | Yield (literature) (%) | Reaction times | | | Ref. |
|---|--|--------------------------------------|------------------------------|---------------------|------------------------|------------------------|-----------------|
| | | | | Microwave reflux | Conventional reflux | Microwave autoclave | |
| $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, PPh_3 | $\text{RuCl}_2(\text{PPh}_3)_3$ | MeOH | 85(74) | 30 min | 3 h | | 8 |
| $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ cyclohexadiene | $[\text{RuCl}_2(\eta\text{-C}_6\text{H}_6)]_2$ | EtOH | 85(95) | 30 min | 4 h | < 1 min | 9 |
| $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ α -phellandrene | $[\text{RuCl}_2(\eta\text{-cymene})]_2$ | EtOH | 67(65) | 10 min | 4 h | < 1 min | 9 |
| $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ cyclooctadiene | $[\text{RhCl}(\text{cod})]_2$ | EtOH/ H_2O (5/1) | 87(94) | 25 min | 18 h | < 1 min | 10 ^a |
| KReO_4 , PPh_3 | $[\text{ReOCl}_3(\text{PPh}_3)_2]$ | EtOH/ H_2O (10/1) | 94(95) | 30 min | 5 h | | 11 |

^a In our hands the conventional synthesis of $\text{ReOCl}_3(\text{PPh}_3)_2$ required 5 h to give good yields, although shorter reaction times were reported in this paper.

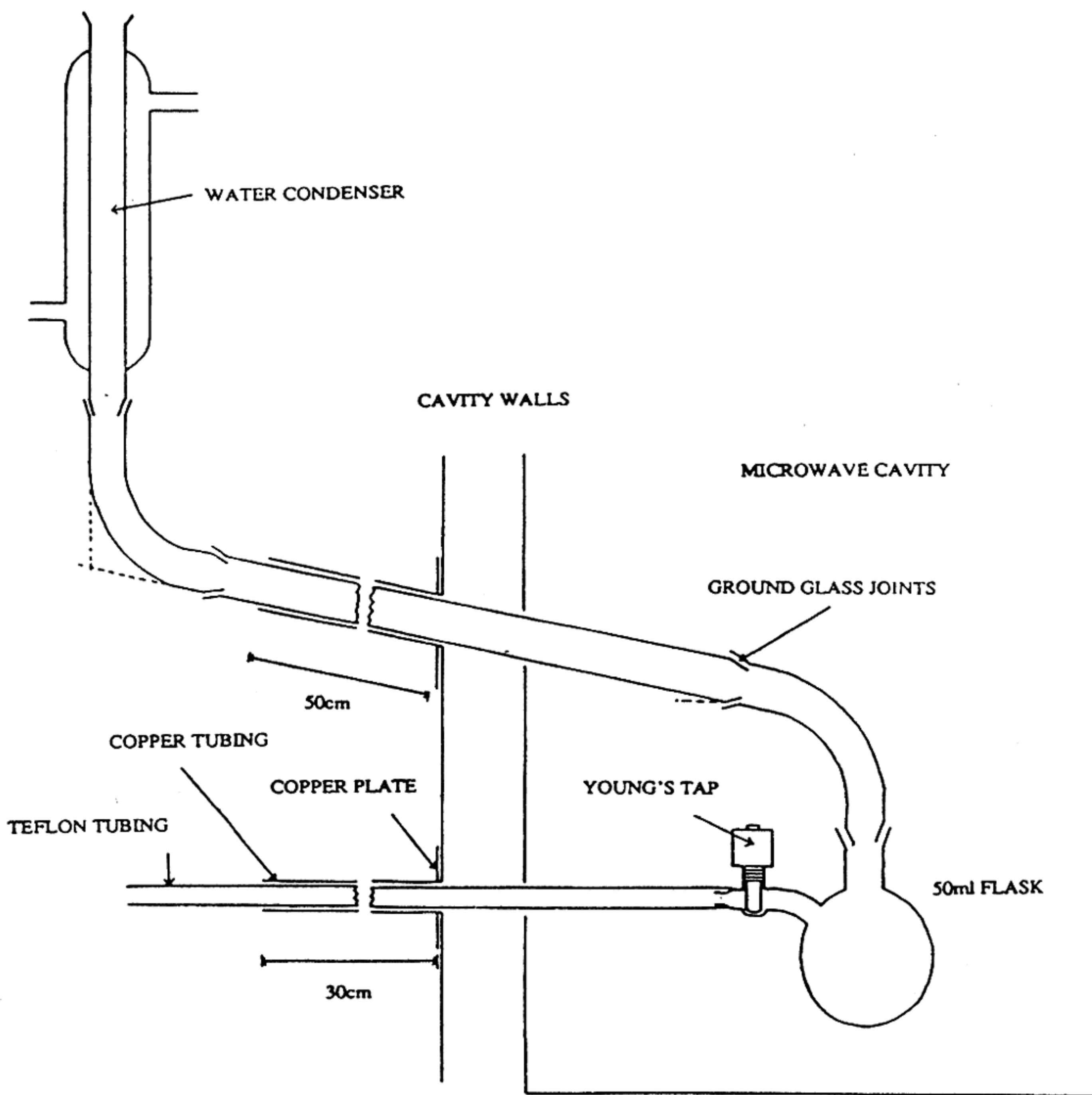


Fig. 1. Modified microwave heating system applied.

waves strongly, e.g. a non-polar organic or inorganic solvent with a low dielectric loss. We have not used this technique, however, but instead have developed an alternative approach based on placing the water-cooled reflux condenser outside the microwave cavity. The condenser is connected to the reaction vessel by means of a port which ensures that microwave losses are kept to a safe limit and the volatile solvents do not pose a hazard.

In this modification, which is illustrated in Fig. 1, the solution is contained within a glass round-bottom flask, which is connected by ground glass joints to a reflux air condenser and a water-cooled condenser. The air condenser passes through a copper tube bolted to the side of a conventional microwave oven, and is connected to the water condenser located completely outside the microwave cavity. This allows the solutions to heat up rapidly when the microwave source is switched on and to reflux safely without a build up of pressure and the release of volatile solvents into the atmosphere. The atmosphere in the round bottomed flask can be controlled by means of a Teflon tube inlet through the side of the microwave cavity. This tube is connected on the outside to an inert gas supply and inside the cavity to the round bottomed flask. Both the air reflux condenser and the Teflon gas inlet tubes lie in copper tubes that are bolted to the walls of the microwave oven and are earthed. These copper 'chokes' prevent the leakage of microwaves from the microwave oven. The apparatus was shown to be safe by using a hand held microwave leakage

detector capable of detecting microwave power levels greater than 1 mWatt/cm² [6]. The dimensions of the tubes are indicated in Fig. 1. Shorter 'chokes' containing ferroelectric materials which absorb microwaves strongly could be designed without compromising the safety aspects of the modification.

Experiments with pure solvents have demonstrated that the temperature of the solvent at the reflux condenser is the normal boiling point, and within the round bottom flask is within 5° of the boiling point. The latter was estimated by using capillary tubes containing organic solids with melting points on either side of the reflux temperature. Thus the dielectric loss heating effects resulting in the rapid heating of the solvent do not create dramatic super-heating effects in the reaction flask. The reflux apparatus is most effective when used for pure solvents or mixtures of solvents with a high room temperature dielectric loss factor, i.e. generally solvents with a high dielectric constant. No heating effects are observed for dry non-polar solvents. At microwave power levels of 250–350 Watts smooth refluxing of the solvent is achieved in less than a minute.

Table 1 provides some examples of reactions carried to completion in the modified apparatus. Table 1 also includes reaction times established when conventional conductive heating techniques were used and for some of the reactions the completion times previously reported [3] for reactions in a Teflon autoclave. The reaction times for the modified reflux apparatus are longer than those obtained in the Teflon containers, in which the temperature is sometimes more than 100° higher than the reflux temperature because of the high pressures induced, but they are frequently much shorter than those achieved with conventional heating techniques. It is possible that localised super-heating effects resulting from the effective coupling of polar molecules in the reaction medium with the microwave radiation may be responsible for these observations. Similar results have been observed in the dissolution of geological and biological samples [7] where processing times have been significantly reduced from hours to minutes by microwave heating in open vessels.

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