

유기초음파화학, 초음파를 이용한 활성이 큰 마그네슘, 아연가루의 제법

韓 秉 熙

충남대학교 이과대학 화학과

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Organic Sonochemistry. Ultrasound Acceleration of the Preparation
of Highly Active Mg and Zn Powders

Byung Hee Han

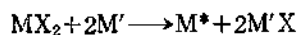
Department of Chemistry, Chungnam National University

Daejeon 300-31, Korea

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The reaction of organic and inorganic substrate at a metal surface, either in a catalytic fashion or in an oxidation addition reaction with consumption of the metal, represents an extremely important area of chemistry. For example, the Reformatsky reaction and Grignard reaction are sometimes difficult to optimize because of reduced activity of the metals. The literature records many attempts to improve these reactions¹⁻⁵. For both of these reactions, one of the most important modifications has been to use of the form of a freshly prepared powder generated from MgCl₂ or ZnCl₂ and potassium or lithium.

This approach developed by Rieke and coworkers produced very active metal that leads to high yields under mild conditions.⁶



M=Mg, Zn. M'=K, Na, Li.

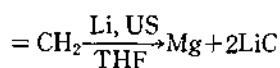
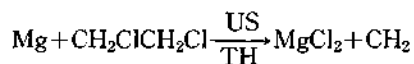
M*=very finely divided Mg, Zn

This modification, while a major improvement over earlier methods, suffers from the necessity of making the metal powder by heating its halide

salts for 8~24 hours with lithium, sodium or potassium in boiling solvent (100~150°C). The first example of sonically accelerated reductions of metal salts that permit the generation of zinc and magnesium powders in less than one hour at room temperature are described.

For example, highly reactive magnesium powder is readily prepared by the sonochemical reduction of anhydrous magnesium chloride with 2.1 equivalent of lithium dispersion in freshly distilled THF under a nitrogen atmosphere. The solution is sonicated with ultrasound laboratory cleaner (50KHz, 117V, 150W, 50/60Hz) for 15 minutes to complete the reduction. When sonication is stopped, the very finely divided black magnesium particles settle out, leaving a clear colorless solution above the black powder.

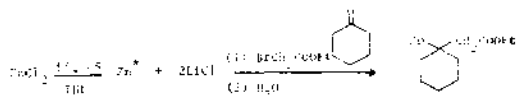
Use of commercially purchased magnesium chloride leads to a magnesium powder of much reduced reactivity. Sonic preparation of anhydrous magnesium chloride is simply sonic reaction of magnesium and excess 1,2-dichloroethane in THF.



US=Ultrasound

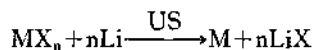
Highly divided fine magnesium powder and very short reaction times are the obvious advantages over Rieke method^{6,7}. The use of naphthalene and diglyme are eliminated. The use of potassium iodide and potassium are also unnecessary. Grignard reagents prepared with our activated magnesium react readily with various substrates.

For example, reaction of *p*-bromoethylbenzene with this magnesium powder at 0°C, followed by hydrolysis gave ethylbenzene over 90% yields. These results were similar with Rieke's. The exceptional reactivity of the zinc powder prepared by zinc chloride and lithium is clearly demonstrated by the Reformatsky reaction. The sonochemical reduction of anhydrous zinc chloride with 2.1 equivalent of lithium dispersion in THF yields a finely divided black zinc powder which will react with bromoethyl acetate and a carbonyl compound.



The zinc powder prepared by potassium reduction have been previously shown to be very

useful in the Reformatsky reaction⁸. Similarly, the zinc powder prepared by lithium reduction lead to nearly quantitative yields in this reaction. Whatever the origin of the high feactivity (particle size, surface area, lack of oxide coating, presence of alkali metal sait), it appears the procedures described above are more convenient than any of the other methods discused and suggest that sonic waves provide an easy method for preparing a broad range of metal powder:



M=any main group or transition metal

X_n=halogen

REFERENCES

1. R. C. Fuson, W. C. Hammann and P. R. Jones, *J. Amer. Chem. Soc.*, **79**, 928 (1967).
2. E. Pearson, D. Cowan and J. D. Becker, *J. Org. Chem.*, **24**, 504 (1959).
3. W. L. Respess and C. J. Tanborski, *Organometal. Chem.*, **18**, 263 (1969).
4. R. D. Rieke and S. E. Bales, *J. Amer. Chem. Soc.*, **96**, 1775(1974).
5. R. D. Rieke, *Accou. Chem. Res.*, **10**, 301(1977). and other references therein
6. R. D. Rieke, P. T. J. Li, T. P. Burns and S. T. Uhm., *J. Org. Chem.*, **46**, 4324 (1981).
7. D. S. Kristol, H. Klotz and R. C. Parker, *Tetrahedron Lett.*, **22**, 907 (1981).
8. S. T. Inaba and R. D. Rieke, *Chem. Lett.*, 25 (1984) and other references therein.