Sonochemical Removal of Adsorbed Water and Alcohol from Magnesium Surfaces

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Ultrasonic radiation has been used increasingly to facilitate heterogeneous reactions [1]. Low intensity sonication (LIS) promotes formation and reaction of organolithium [1, 2] and organomagnesium [2] reagents. The question has been raised whether sonication promotes reactivity in soft metals by causing surface dislocations [2]. The cavitation phenomenon [3] could cause surface dislocations by its combined abrasion, thermal, and/or pressure effects [4]. Our results below support LIS removal of surface adsorbed water/alcohol as the primary mechanism of sonochemical magnesium activation.

Gilman and Vanderwal found that water affects directly the induction period for reaction of magnesium with 1-bromobutane in ethyl ether [5]. We have measured the induction period for reaction of magnesium with 2-bromopentane both with and without LIS. Results are shown in Table I.

In the standard reaction, magnesium turnings (1.34 g, 55.1 mmol) and ethyl ether (7.0 ml) were added to a 100 ml round bottom flask. The system was fitted with reflux condenser, dropping funnel, and $CaCl_2$ drying tube. The flask was lowered into an ultrasonic cleaning bath (50 °C, 125 W, 50 kHz) or heating bath (50 °C). When the mixture reached reflux 2-bromopentane (20 drops) was added. When the first greying of solution appeared, evidencing reaction initiation, additional 2-bromopentane (7.55 g, 50 mmol total) in ethyl ether (23 ml) was added. The mixture was allowed to reflux for 45 minutes after initiation. The yield of 2-pentylmagnesium bromide was determined by titration using the method of Gilman, *et al.* [6].

From Table I it can be seen that, with standard anhydrous ethyl ether, application of ultrasound speeds markedly the time required for initiation. With ethyl ethers containing larger quantities of water and alcohol, ultrasonic waves promote initiation in $\leqslant 8$ minutes. The purely thermal reactions do not initiate in from one to three hours and will begin only when a piece of magnesium is crushed manually. The longer induction periods (both thermally and sonochemically) with greater water/alcohol content point to water/alcohol adsorption playing a major role in limiting magnesium reactivity.

When magnesium turnings in ether or hexane are subjected to prior sonication for extended periods of time (up to 2 hours), their reactivities as measured by induction periods are unchanged when allowed to react in the solvents and conditions listed in Table I. Thus, lattice defects and dislocations, cited as possible important factors in magnesium reactivity, do not appear to be induced by LIS to an extent necessary to cause reactivity with alkyl halide. Similarly, removal of surface oils or oxide coating does not appear to be initiation limiting.

Sonication does not significantly alter yields of the reactions. Some water/alcohol does reduce yield, perhaps through hydrolysis of the alkyl halide or irreversible reaction with magnesium.

The above technique has been used in our general laboratory work to initiate reluctant Grignard reac-

TABLE I. Induction Periods and Yields for Reaction of Magnesium and 2-Bromopentane in Ethyl Ether with Varying Water/Alcohol Content.

Ethyl ether	Treatment[a]	Induction period[b] (min)	Yield[b] (%)
Anhydrous[c]	T	6–7	67
Anhydrous[c]	S	<0.17	65
Reagent[d]	T	120–180[e]	54
Reagent[d]	S	3–4	53
Half saturated[f]	T	60–180[e]	58
Half saturated[f]	S	6–8	54

[a]T = thermal, S = sonochemical. [b]Results are an average of three independent determinations. Induction periods and yields were not altered when reactions were carried out under dry N_2. [c]Contains 0.01% H_2O, 0.01% EtOH. [d]Contains 0.5% H_2O, 2% EtOH. [e]Reaction initiated only upon mechanical crushing of the magnesium at the time indicated. [f]Prepared by adding excess water to anhydrous ethyl ether, separating layers, and diluting the resulting wet ether with equal parts anhydrous ethyl ether.

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tions. We are currently studying poison stripping from heterogeneous catalyst surfaces with LIS and high intensity sonication.

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References

1 P. Boudjouk, B.-H. Han, and K. R. Anderson, *J. Am. Chem. Soc., 104,* 4992 (1982), and references therein.
2 J.-L. Luche and J.-C. Damiano, *J. Am. Chem. Soc., 102,* 7926 (1980).
3 H. Alliger, *Amer. Lab., 7*(10), 75 (1975).
4 D. S. Kristol, H. Klotz, and R. C. Parker, *Tet. Lett.,* 907 (1981).
5 H. Gilman and R. J. Vanderwal, *Recl. Trav. Chim. Pays-Bas, 48,* 160 (1929).
6 H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc., 51,* 1576 (1929).