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Visualization of the Areal Distribution of the Reactivity of Magnesium Surfaces in the Formation of Grignard Reagents

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Summary: Magnesium surfaces are photographed *in situ* during the formation of Grignard reagents (in the presence of an indicator) in order to study the mechanism and to understand the reactivity of magnesium surfaces.

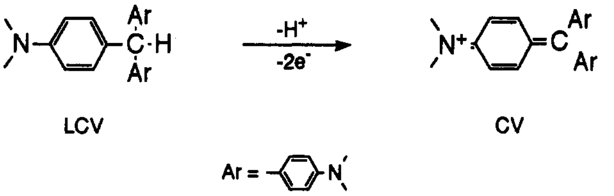
The Grignard reagent is one of the most important and versatile reagents for synthetic chemistry. Thus, it is not surprising that the mechanism of its formation has been widely studied.[1] Although there is agreement on the overall mechanism, the nature of the radical intermediate is widely debated.[2,3] Evidence has been provided for both a freely diffusing radical as well as a surface-bound radical. Garst, et al.[3] elegantly supported the hypothesis of freely diffusing radicals by modeling all possible competing reactions and predicting product distributions from reaction rates. Agreement between predicted and experimental yields was excellent.[3] However, patterns of reactivity on a surface can affect concentration gradients and competition between first- and second-order reactions;[4] Garst et al. have assumed a uniformly reactive surface and linear diffusion in their model. Evidence presented by Hill et al.[5] suggests that most of the magnesium surface is unreactive and that the organomagnesium halide is produced at relatively small reactive sites.

Patterns of reactivity on electrode surfaces have been photographed by electrochemically oxidizing luminol; only reactive sites are illuminated by chemiluminescence.[6] In this paper we describe a system for *in situ* visualization of patterns of reactivity of a magnesium surface in the formation of Grignard reagents.

Reactions were performed in a Teflon flow cell which includes a slot covered with a microscope slide.[7] Magnesium ribbon is placed in the slot and can be viewed or photographed *in situ* through the microscope slide.

We have found that leuco crystal violet (LCV, 4,4′,4″-methyldiynetris(*N*,*N*-dimethylaniline)) in the presence of oxygen is an excellent indicator for Grignard reagents. When a solution of (4-methylphenyl)magnesium bromide is added to a solution of LCV, a deep blue solution results. Products are crystal violet (by spectroscopy, $\lambda_{max} = 594$ nm with a shoulder at 560 nm) and toluene (by GC, 50% yield). If the reaction is performed under Ar, the deep blue color is not observed until prepurified oxygen is bubbled through the solution. These observations are consistent with the mechanism proposed in Scheme I where the organomagnesium halide acts as a base and oxygen as the oxidizer.[8] LCV is an excellent indicator because it is colorless while the crystal violet is very dark blue.

Scheme I



In a typical experiment in the flow cell, bromoethane (1.85 mL, 25 mmol) and LCV (5 mg, 0.013 mmol) are dissolved in THF (10 mL), and this solution is injected into the flow cell. Observations are made under static (no flow) conditions. After several minutes, dark blue spots appear on the magnesium surface. We attribute this to production of the Grignard reagent at spots on the surface, followed by conversion of LCV to crystal violet. Early in the reaction, sites as small as 30 μm are observed. When the solution in the cell becomes so darkly colored that the surface is no longer visible, fresh solution is flowed through the cell.

Alternatively, if iodoethane is reacted with magnesium, a dark orange-brown precipitate forms at reactive sites.[9] However, the surface eventually becomes covered with the precipitate, and further patterns of reactivity are not evident.

Finally, it is possible to see the reactivity simply by watching holes form in the magnesium as the Grignard reagent is formed. This is similar to the study by Hill et al.[5] except that in this case the reaction is monitored *in situ*. Although the absence of indicator simplifies the experiment,[10] the holes are not as evident in color photography as the appearance of crystal violet. Also, continued reactivity at a hole is only apparent by increasing hole size. On the other hand, this method is better for measurement of reactive site size.

Figure 1 is an *in situ* photomicrograph of a magnesium surface after 38 min of reaction with bromoethane. It is

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(1) (a) Walborsky, H. M. *Acc. Chem. Res.* **1990**, *23*, 286. (b) Garst, J. F. *Acc. Chem. Res.* **1991**, *24*, 95

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(3) (a) Garst, J. F.; Swift, B. L.; Smith, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 234. (b) Garst, J. F.; Swift, B. L. *J. Am. Chem. Soc.* **1989**, *111*, 241.

(4) Amatore, C.; Saveant, J. M.; Tessier, D. *J. Electroanal. Chem.* **1983**, *146*, 37.

(5) Hill, C. L.; Vander Sande, J. B.; Whitesides, G. M. *J. Org. Chem.* **1980**, *45*, 1020.

(6) (a) Engstrom, R. C.; Johnson, K. W.; DesJarlais, S. *Anal. Chem.* **1987**, *59*, 670. (b) Bowling, R. J.; McCreery, R. L.; Pharr, C. M.; Engstrom, R. C. *Anal. Chem.* **1989**, *61*, 2763. (c) Engstrom, R. C.; Ghaffari, S.; Qu, H. *Anal. Chem.* **1992**, *64*, 2525.

(7) A groove (2.3 × 0.4 × 0.25 cm) was cut in a block of Teflon (PTFE, 5 × 2.5 × 0.6 cm), and a microscope slide was clamped over the groove using Teflon tape as a gasket. Two holes were tapped through the back of the block, and 0.4-cm o.d. Teflon tubing was connected for flowing solutions through the cell.

(8) In the absence of alkyl halide, no reaction between LCV, magnesium, and oxygen is apparent either by color development or by pitting of the magnesium surface.

(9) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954.

(10) Corrosion of the magnesium is not apparent in the absence of alkyl halide, and the presence of oxygen is not necessary for this experiment. These latter two methods of detecting reactive sites (by pit formation or with iodoethane) require neither indicator nor oxygen, yet they yield results similar to those when the sites are indicated by LCV. This confirms that the indicator does not participate in or change the mechanism of the formation of alkylmagnesium halide.

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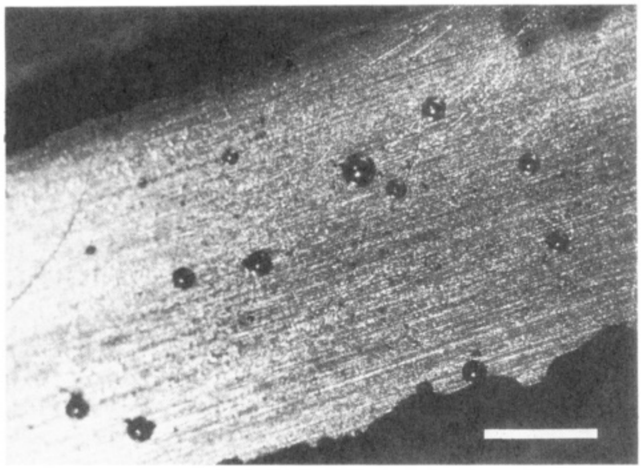

Figure 1. *In situ* photomicrograph of magnesium surface after 38 min of reaction with bromoethane. Scale bar = 1 mm.

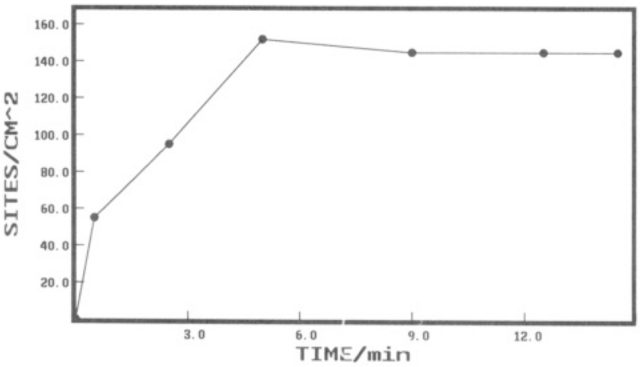

Figure 2. Density of reactive sites vs time of reaction. Reaction with bromoethane in the presence of LCV.

readily apparent that the magnesium surface is largely unreactive and that the reaction mostly proceeds by the growth of relatively few reactive sites. Figure 2 is a plot of reactive site density vs time of reaction prepared using LCV as an indicator. It can be seen that the number of sites increases rapidly for a short time after initiation of the reaction and then remains constant or slightly decreases as sites grow to the point of overlap. Figure 3 indicates the rate of growth of five separate sites.[11] *In situ* measurement is necessary to obtain these data because of the stochastic nature of initiation of Grignard reactions.[5]

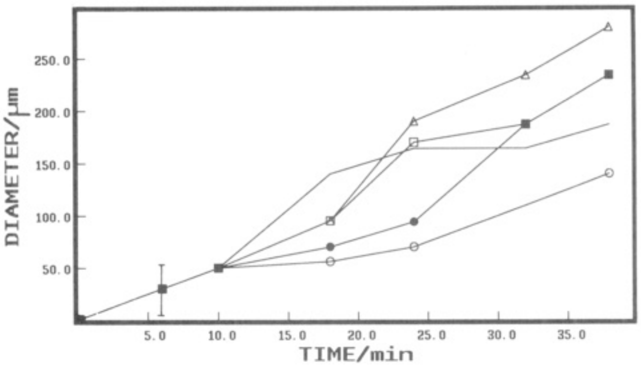

Figure 3. Size of reactive sites vs time of reaction (five different sites plotted). Reaction with bromoethane.

These observations indicate that, early in the reaction of alkyl halides with magnesium, reactive sites are quite small and diffusion of reactants and products is spherical rather than linear. As the sites grow larger, convection and linear diffusion contribute significantly and mass transport is very complex. Concentration gradients influence the outcome of competition between first- and second-order reactions, so it is remarkable that a model assuming linear diffusion can so accurately predict product ratios.[3,12]

We intend to use this technique to quantify site initiation and growth in order to test hypotheses concerning what determines site reactivity and product distribution. Also, we will compare the reactivity of various preparations of magnesium surfaces (e.g., Rieke Mg, chemically polished[5] Mg, Mg powder).

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Supplementary Material Available: Experimental details (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) These data should be viewed as only semiquantitative. Because the volume of the reaction vessel is small, it contains less than 1 equiv of alkyl halide relative to magnesium. Although fresh solution is flowed into the cell several times over the course of an experiment, depletion of alkyl halide by as much as 20% is possible, so the concentration of alkyl halide is only approximately known. Furthermore, there is no forced convection in the cell (except for the brief periods when the solution is flowing), so the reaction proceeds more slowly than under typical synthetic conditions.

(12) Ashby, E. C.; Oswald, J. *J. Org. Chem.* **1988**, *53*, 6068.