Reactivity of Magnesium Surfaces during the Formation of Grignard Reagents

Cynthia E. Teerlinck and Walter J. Bowyer*

Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York 14456

Received September 6, 1995[⊗]

A reaction cell which allows for photomicrographic observation of magnesium surfaces during formation of Grignard reagents is described. As the reaction proceeds, a finite number of discrete sites initiate relatively rapidly. Following this stage, the reactive area increases by the growth of sites rather than by the initiation of new sites. Sites are randomly located across the magnesium surface (neither clustered nor dispersed) consistent with their formation at crystalline defects or metallic impurities. Various methods of magnesium surface activation are tested. For example, iodine and ferric chloride increase reactivity by increasing the density of reactive sites and by increasing the rate at which individual sites react. Scratching the magnesium surface increases reactivity by decreasing the time required for initiation of reactive sites. A mercury/magnesium amalgam provides a uniformly reactive surface, but the reaction rate is very slow.

Introduction

Because of their ability to act as both bases and nucleophiles, the organomagnesium halides comprise one of the most important and versatile classes of reagents, the Grignard reagents. Almost a century after their description, the mechanism of formation of Grignard reagents from organohalides and magnesium metal is still actively debated.[1−14] Evidence has been presented which is consistent with electron transfer from the magnesium to the organohalide to form a radical anion. This radical anion cleaves rapidly to form a halide anion and an organic radical (Scheme 1).

Scheme 1

$$RX + e^{-} \rightarrow R^{\bullet} + X^{-}$$

The surface nature of the radical is actively debated. While retention of configuration and other experiments suggest a surface bound radical,[1,2] distribution of products is consistent with a freely diffusing radical.[3−6]

Just as the surface creates theoretical difficulties at the molecular level, the magnesium surface also creates the largest difficulty on the macroscale. Initiation of Grignard reactions can be difficult,[5,7−10] and organic textbooks describe a variety of surface treatments which have been found empirically to activate the magnesium surface.[15] Even under rigorously dry conditions, the progress of Grignard reagent formation can be drastically affected by surface preparation. For example, finely divided "Rieke" magnesium is more reactive than magnesium turnings.[16]

Metal surfaces are notoriously difficult to prepare reproducibly,[17] so it is not surprising that Grignard reactions are sometimes irreproducible and difficult to initiate. Surface oxides, adsorbed insulating layers, and crystal lattice orientation can all affect heterogeneous reaction rates.[17−20] The effects of surface preparation on heterogeneous rate constants have been widely studied for electrodes, but electroanalytical tools are rarely applicable to the study of chemical reactions at metal surfaces (such as Grignard reagent formation). However, *in situ* observation of reactivity is possible.

The chemiluminescence produced by the oxidation of luminol at an electrode surface has been used for visualization of patterns of reactivity on electrode surfaces.[19,20] The unilluminated electrode surface is viewed with a microscope. Where the oxidation of luminol occurs, sites on the surface are illuminated by the resulting chemiluminescent reaction, allowing photomicrography of the patterns of reactivity. Resolution of sites smaller than 10 μm is possible.[20] These studies have been important in understanding patterns of reactivity on electrode surfaces.

We have used a similar strategy for studying the formation of Grignard reagents. In an earlier communication, we briefly described Grignard reagent formation in a reaction cell which allowed *in situ* observation of the magnesium surface.[21] By photomicrography of the mag-

---

* To whom correspondence may be addressed: bowyer@hws.edu; 315-781-3608; fax 315-781-3587.

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

(1) Walborsky, H. M.; Topolski, M. *J. Am. Chem. Soc.* **1992**, *114*, 3455.

(2) Rachon, J.; Walborsky, H. M. *Tetrahedron Lett.* **1989**, *30*, 7345.

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

(4) Garst, J. F.; Swift, B. L. *J. Am. Chem. Soc.* **1989**, *111*, 241.

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

(6) Garst, J. F.; Ungváry, F.; Batlaw, R.; Lawrence, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 5392.

(7) Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217.

(8) Rogers, H. R.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 226.

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

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

(11) Bodewitz, H. W. H. J.; Blomberg, C; Bickelhaupt, F. *Tetrahedron* **1975**, *31*, 1053.

(12) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4284.

(13) Molle, G.; Bauer, P.; Dubois, J. E. *J. Org. Chem.* **1982**, *47*, 4120.

(14) Rogers, H. R.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 231.

(15) For example: Williamson, K. L. *Macroscale and Microscale Organic Experiments*; D. C. Heath: Lexington, MA, 1989.

(16) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

(17) Hubbard, A. T. *Acc. Chem. Res.* **1980**, *13*, 177.

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

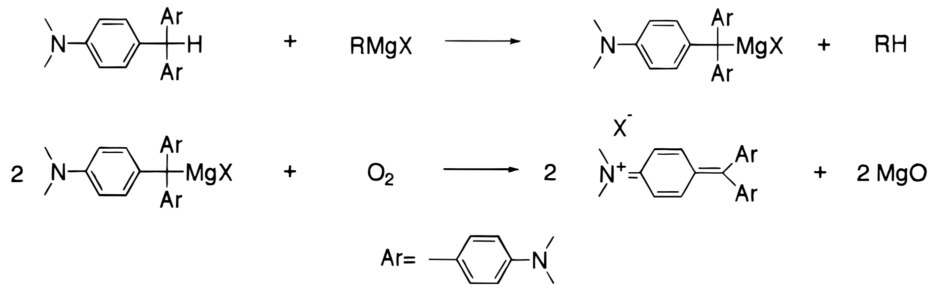
(19) Engstrom, R. C.; Johnson, K. W.; DesJarlais, S. *Anal. Chem.* **1987**, *59*, 670.

(20) Bowling, R. J.; McCreery, R. L.; Pharr, C. M.; Engstrom, R. C. *Anal. Chem.* **1989**, *61*, 2763.

(21) Koon, S. E.; Oyler, C. E.; Hill, J. H. M.; Bowyer, W. J. *J. Org. Chem.* **1993**, *58*, 3225.

0022-3263/96/1961-1059$12.00/0 © 1996 American Chemical Society

Scheme 2



nesium surface during Grignard reagent formation (with and without a colored indicator), patterns of surface reactivity were observed. Consistent with earlier *ex situ* observations,[9] we showed that the surface reacted at discrete sites. In this paper we test various hypotheses in an attempt to explain why certain areas of the surface are reactive while others are not. Also, we observed reactivity after a variety of chemical and physical treatments of the magnesium surface. The rate of initiation, density of sites, and rate of the reaction for the treated areas were compared to those of untreated magnesium surfaces.

Results and Discussion

Indicators. Several methods of revealing reactive sites were tried. Chemiluminescence associated with Grignard reagents seemed ideal since the luminescence is detected on a dark background. Also, excited states are short-lived, so diffusion away from the site of production (which would decrease resolution) is not significant. Although we tried two chemiluminescent reactions (reaction of Grignard reagents with either oxygen or nitrobenzene), both were too dim for *in situ* photography of Grignard reagent formation.

Visible indicators are a useful alternative to chemiluminescence for revealing reactive sites. In order to detect reactive sites on a magnesium surface, it is optimum to have an initially colorless indicator become very dark in the presence of Grignard reagents. We found that leucocrystal violet (LCV) reacts with Grignard reagents to produce crystal violet (CV). LCV is colorless, so the initial solution does not obscure the magnesium surface. CV is so darkly colored that it is easily seen even at submillimolar concentrations in very thin layers of solution.

In order to propose a mechanism for the reaction of LCV with Grignard reagents, we analyzed products of the reaction of LCV with *p*-tolylmagnesium bromide. When THF solutions of each were mixed in the presence of oxygen, a very dark blue solution resulted. By GC analysis, toluene was produced in 50% yield. The solution was analyzed for crystal violet by UV-visible spectroscopy after 1:500 dilution. The peak at 594 nm with a shoulder at 560 nm was characteristic of CV, and the yield was at least 50%. (Some CV precipitates out at these concentrations and was not analyzed for, so 50% is the minimum yield.) Excess Grignard reagent (to 10 equiv) does not destroy the color of CV (a necessary condition if the indicator is to be used at concentrations very small relative to the Grignard reagent being produced).

If the Grignard reagent and LCV were mixed in the absence of oxygen, a yellow solution resulted. However, introduction of either air or prepurified oxygen rapidly converted the yellow solution to the blue of CV. The yield of toluene was unaffected by whether oxygen was present initially or was introduced after mixing the solutions.

All of these results are consistent with the mechanism proposed in Scheme 2. The organomagnesium halide acts as a base to abstract a proton from LCV. The resulting anion is then oxidized by oxygen to produce the highly colored cation, CV. No *p*-cresol or bitoluyl was detected by GC, suggesting that under these conditions direct oxidation of the Grignard reagent is not a significant problem.

The use of visual indicators to quantify reactive sites is fundamentally limited in resolution by diffusion of the products. After the indicator is produced at a reactive site, it may slowly diffuse away from that site. Furthermore, we initially feared that the indicator, even at the very low concentrations used, affected the progress of Grignard reagent formation.

Therefore, in addition to using LCV as an indicator, two direct methods for detecting reactive sites also were used. When iodoethane is reacted with magnesium, a brown-orange precipitate is deposited on the magnesium surface presumably at active sites.[10] Unfortunately, this method is limited after a short while by the encrusting of the surface with a thick layer of precipitate. However, results early in the reaction are consistent with those observed using LCV as a indicator.

The final method for detecting discrete reactive sites is the simple observation of the formation of pits in the magnesium surface during Grignard reagent formation. This technique is limited since pits will not form in a uniformly reactive surface. However, under most conditions pitting of the surface is obvious.

We have found the use of LCV as an indicator and the observation of pit formation in the magnesium surface to be complementary techniques. In this paper we describe results from both methods, the choice depending on the particular experiment and magnesium surface preparation. Using these techniques separately, we have also confirmed that LCV does not affect the reactivity of the magnesium surface.

Observations of Reactivity on Polished Magnesium. Our initial observations were made on magnesium strips (99.9+%) which had been manually polished to uniform reflectivity. When THF solutions of alkyl halide contacted the magnesium surface, discrete reactive sites on a largely unreactive magnesium surface were indicated by all three techniques (LCV, iodoethane, and pit formation). In about 80% of the trials, initiation of the reaction was apparent within 1 min by the rapid formation of very small (<25 μm) reactive sites. Figure 1 (top photomicrograph) illustrates the hemispherical pits resulting from reaction with bromoethane.

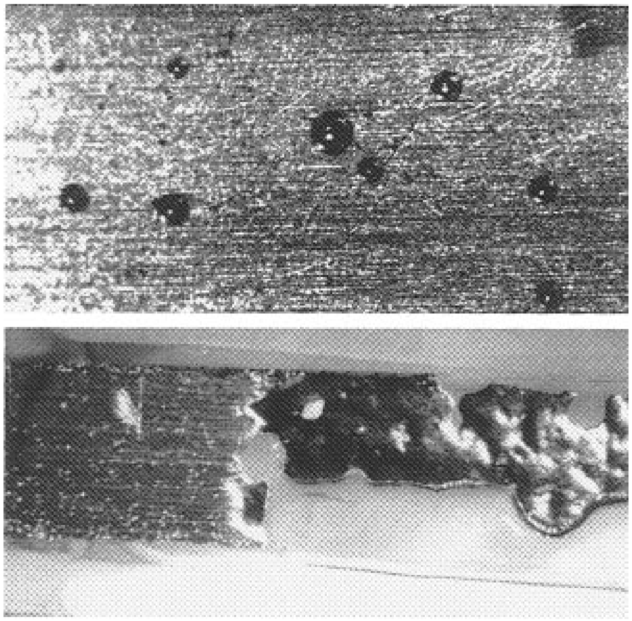


Figure 1. Upper photograph: Magnesium surface after reaction with bromoethane. The width of field is 4.3 mm. Lower photograph: Magnesium surface after reaction with bromoethane. Left side is untreated; the right side was treated with 2% $FeCl_3$ in THF. The width of field is 11.8 mm.

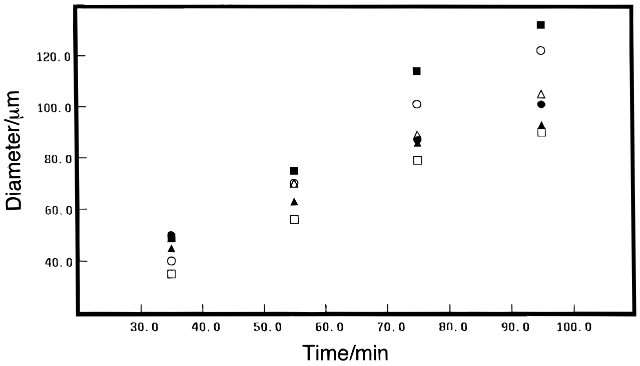


Figure 2. Plot of diameter (μm) vs time for six different pits in a magnesium surface during reaction with 1.0 M bromoethane in THF.

One advantage of *in situ* observation is the ability to observe each site as it grows. Figure 2 is a plot of the diameter of six different pits in a magnesium surface as a function of time during reaction with 1 M bromoethane. This method allows us to compare relative rates of reactions under different conditions (e.g. different surface treatments, *vide infra*). We have measured the rate of the reaction of 2.5 M bromoethane with magnesium on eight separate occasions and have measured an average rate of growth (the slope of a plot of diameter vs time) of 5.0 μm/min with a standard deviation of 33%. Within a single experiment, standard deviation between pits is about 20% (we typically measure 10 pits in a single experiment).

A plot of the density of sites vs time shows that after 4−8 min no new sites are initiated. Beyond this time, continued reactivity occurs solely by growth of sites established early in the reaction. With time, the density of reactive sites decreases as sites begin to coalesce (of course total reactive area increases continuously).

We have found that the density of reactive sites is highly variable between nominally identical experiments. The plateau of plots of density vs time ranged between 65 and 2400 sites/cm^2 for six different experiments. To test whether this variation was due to daily variations in our experiments (e.g. variations in residual moisture), we reacted long strips of magnesium (3 × 70 mm) in a 100 mm Schlenck tube containing 10 mL of the THF/alkyl halide/LCV solution. After 10 min, we removed the strips, rinsed them, and measured the density of pits. We found that the density was as variable over the length of a single strip as it was between different *in situ* measurements. This suggested that the variability was largely due to variations in the surface (we discuss this further below).

Table 1. Statistical Comparison of Site Distribution on a Magnesium Surface to a Random Distribution

no. of sites/quadrat	experimental frequency (f)	Poisson frequency (F)	$(f - F)^2/F$
0	46	48.3	0.1095
1	56	53.1	0.1584
2	33	29.2	0.4945
3	6	10.7	2.064
>3	4	3.7	0.0243
total	145	145	$\chi^2 = 2.851$

Several hypotheses are possible explanations for reactive site formation on an apparently uniform surface. It is possible that when an area of magnesium is reacting vigorously, the reaction in neighboring areas is inhibited, either by concentration or voltage polarization. For example, exclusion zones around corrosion pits[22] and nucleation sites[23] have been described.

To test for this in the formation of Grignard reagents, we analyzed the areal distribution of reactive sites. We surveyed photographs of reactive surfaces into 0.5 mm quadrats. The number of quadrats containing 0, 1, 2, 3, or more than 3 sites was censused. A Poisson distribution was then used to generate the frequency of occupation expected if reactive sites were randomly distributed over the surface.[24] Data for a typical experiment are tabulated in Table 1. The experimental and expected frequencies were compared (by χ^2 analysis), and we detected no significant difference from a random distribution for four separate experiments. If reactivity in one area inhibited reactivity in neighboring areas, "exclusion zones" would be indicated by a larger frequency of singly occupied quadrats and a lower frequency of unoccupied quadrats than expected for a random distribution. Thus, these data indicate that discrete reactive sites on the magnesium surface cannot be explained by a suppression of reactivity near the sites.

Alternatively, if products or intermediates increase the reactivity of a magnesium surface, one might predict discrete reactive sites. Once an area began reacting, the reaction would be accelerated, forming highly reactive sites relative to more distant areas. We tested this hypothesis in two ways. First, we would predict a clumped distribution if this were true. In other words, quadrats containing one reactive site would be likely to form additional sites. If this were true, a lower frequency of singly occupied quadrats and a larger frequency of multiply occupied sites relative to a random distribution would be expected. Again, the random distribution of

---

[22] Milchev, A. *Electrochim. Acta* **1983**, *28*, 947.

[23] Milchev, A.; Kruijt, W. S.; Sluyters-Rehbach, M.; Sluyters, J. H. *J. Electroanal. Chem.* **1993**, *350*, 89.

[24] Salvarezza, R. C.; Arvia, A. J.; Milchev, A. *Electrochim. Acta* **1990**, *35*, 289.

sites is not consistent with this and so does not support this hypothesis.

Also, we performed an experiment where a strip was reacted for 10 min with bromoethane. The reaction was then interrupted by flowing 20 mL of pure THF through the cell to rinse the strip. The bromoethane solution was then reintroduced, and reactivity was monitored. In an area of 0.40 cm^2, 144 sites formed in the first 10 min and 131 (91%) continued reacting after the rinse. That 91% of the sites continued to react after the rinse suggests that products or intermediates in solution are not responsible for continued reactivity at the sites.

It has been suggested that the formation of Grignard reagents is initiated at crystal dislocations on the magnesium surface.[9,10] Alternatively, microcrystalline impurities in the magnesium surface are suspected to be initiation sites. The random distribution of sites on the surface is consistent with these hypotheses. Our observation that few new sites form after the reaction is underway is also consistent with these hypotheses.

As the reaction proceeds, the dislocation or impurity is oxidized away, and the site becomes a smooth hemispherical pit with a uniformly reactive surface. Presumably, this smooth surface, although it is free of crystal dislocation, continues to react because it is pristine, freshly exposed metal.

Observations of Reactivity after Surface Treatment. In order to further test the hypothesis of initiation at crystal imperfections or impurities, we investigated magnesium surfaces after various physical and chemical treatments. We also hoped to understand the mechanisms by which certain surface treatments increase the reactivity of magnesium toward Grignard reagent formation. For the following experiments the magnesium strip was manually polished as described above. Then, one half of the strip was treated while the other half acted as an internal control.

(a) Bent or Twisted Magnesium. In one of our experiments, we observed that a magnesium strip which had been inadvertently bent in assembling the reaction cell was much more reactive than typical. Other authors have suggested that magnesium turnings are appropriate for Grignard reactions because the bending causes crystal lattice dislocations where reactive sites can initiate.[9,10] To test the effect of crumpling magnesium, we bent a strip of magnesium into an accordion-like structure, leaving a portion of the strip flat as a control. We performed this experiment five times and found that bending the magnesium increased reactivity dramatically in three of them. Reactivity was increased by an increase in both reactive site density and the rate of growth of the sites both on the outside and inside of the folds (relative to the portion of the strip which had not been bent). The increase in site density is consistent with an increase in crystal dislocations. Also, the stretching of the surface on the outside of the bend may increase reactivity by exposing fresh metal. However, bending the strip did not increase reactivity in two of the five trials.

(b) Scored Surfaces. Surfaces were scored with a stainless steel scalpel to an approximate depth of 0.1 mm on one half of the strip while the other half acted as the control. Although we never observed that sites were more dense or grew faster on the scratched side, reactive sites frequently occurred in the scorings. For example, in one experiment 88% of the reactive sites which formed on the scored half were located within the score marks. However, the score marks only covered 25% of the surface on the treated side. Because the scoring exposes fresh magnesium and presumably causes crystal dislocations, it is not surprising that sites form preferentially in scratches. However, it is surprising that scratching the surfaces does not increase the density of reactive sites.

(c) Chemically Polished Magnesium. Cleaning with 6% aqueous nitric acid removes the outer layer of magnesium and magnesium oxide, exposing fresh metal.[9] However, just as dislocations in the crystal structure are more reactive toward alkyl halides, they are also more easily removed by the acid rinse. We chemically polished approximately one half of a magnesium strip while the other half served as the control. The entire strip was rinsed twice in anhydrous ethyl ether and dried at 80 °C under argon. Chemical polishing increased the time required for initiation and decreased reactive site density. Generally, reactivity was limited to the edges and corners of the chemically polished strip. That this effect is not due to moisture introduced during the polishing or rinse is confirmed by the internal control. For a comparison to an unrinsed magnesium strip, a short piece of chemically polished magnesium was connected to a piece of manually polished magnesium with platinum wire. Similar results to those described above were obtained except that the most reactive area occurred where the platinum wire contacted the magnesium strip. We are investigating further the role of platinum in activation of the magnesium surface.

(d) Ultrasound. We found that treating magnesium with ultrasound for 30 min in dioxane[25] prior to reaction with bromoethane in THF did not significantly increase either reactive site density or rate of growth. In contrast, ultrasound is a well-known means for accelerating the formation of Grignard reagent when applied to the reaction mixture.[5] This suggests that ultrasound accelerates the reaction either by enhanced mass transport and/or by localized high temperatures[26] rather than by an effect on the magnesium surface. (This is in contrast to electrodes for which ultrasound can create reactive sites.[25])

(e) Magnesium Amalgam. Because mercury surfaces are smooth and highly reproducible,[27] we prepared mercury amalgam for reaction with alkyl halides. First we reacted 0.05 M mercuric chloride in THF with the magnesium strip in the reaction cell for 30 min. The mercuric ions were reduced to elemental mercury which was deposited on the surface in an even gray coating. With time, small droplets of mercury formed on the surface. We then rinsed the strip by flushing the cell with 20 mL of THF and introduced the bromoethane/LCV solution. The appearance of the purple color over the entire surface indicated the reaction had initiated within 2 min, however, the reaction was very slow. At no time did we see any evidence of discrete reactive sites—even after several hours no pits had formed.

As an alternative preparation, we dissolved magnesium powder in mercury (2% by weight[27]) and reacted it with the bromoethane/LCV solution in the reaction cell. Consistent with the results for the magnesium surface treated with mercuric chloride, the reaction was very slow but appeared to be uniform over the entire surface.

(f) Iron Trichloride. $FeCl_3$ is known to activate magnesium surfaces.[10] The Fe(III) is reduced to Fe(0)

---

(25) Zhang, H.; Coury, L. A., Jr. *Anal. Chem.* **1993**, *65*, 1552.
(26) Suslick, K. S. *Science* **1990**, *247*, 1439.
(27) Wang, J. *Stripping Analysis: Principles, Instrumentation, and Applications*, VCH Publishers: Deerfield Beach, FL, 1985.

by the magnesium, and the iron crystal on the surface may act as an initiation site. The surface was treated with 2% $FeCl_3$ in THF either by dipping half the strip in the solution or by spotting the surface with 1 μL droplets of the solution. The strip was then briefly dried in the oven and rinsed in the reaction cell with THF immediately before use.

The treated surface showed a dramatic increase in reactivity. Where the iron solution contacted the surface, the density of sites was so high that the entire surface was reactive in less than 4 min, and smooth, uniformly-reactive surfaces resulted. This is illustrated in the lower photomicrograph in Figure 1. The left side (control) shows small, discrete reactive sites. In contrast, the treated side is nearly consumed, and the remaining surface is quite smooth.

Furthermore, the rate of reaction was increased. Treated areas were typically entirely reacted (all magnesium consumed—a reaction depth of 0.17 mm) in about 10 min. In contrast, pits on the control side had reacted to a depth of only about 0.025 mm in the same time—representing a 7-fold increase in rate when magnesium is treated with iron.

The effect of iron was highly localized. The density of reactive sites on the control side of iron-treated strips were not significantly different from those on untreated strips. When the surface was treated in spots, the density of sites was slightly higher very close (<0.5 mm) to the spot, but the rate of corrosion near the treated area was similar to that on untreated strips.

These observations are consistent with the hypothesis of crystalline impurities acting as initiation sites. In addition, the iron acts as a catalyst to increase the rate after a site is initiated. Of course, iron is known to increase side reactions and should be used with caution.[10,28]

(g) Iodine. We have found that reactivity on surfaces treated with 2% iodine in THF is even more dramatic than on those treated with ferric chloride. The increase in rate is comparable for both treatments (corrosion through the 0.17 mm strip is complete within 10 min). However, when a strip is treated in spots with the iodine solution, the strip is activated in areas as much as 2 mm from the spot. We suspect that iodine diffuses from the treated area to the formally untreated areas and so activates them.

We also attempted activation of the magnesium surface with 2% aqueous iodine. We found that the reactive site density and reaction rate were greater after treatment with the aqueous solution than in the control but much less than in an area treated with iodine in THF. In contrast, we found that treatment with aqueous ferric chloride completely deactivated the surface. Apparently, inhibition by reaction with water is more important than the activation by the iron.

Experimental Section

Reagents. HPLC grade tetrahydrofuran (0.003% H_2O) was purchased from Fisher Scientific and stored under argon. Alkyl halides were purchased from Aldrich and used without further purification. 4,4′,4″-Methylidynetris(*N*,*N*-dimethylaniline) (leucocrystal violet, LCV) was purchased from Pfaltz and Bauer. Purification of THF and alkyl halides sometimes decreases initiation time, but does not change the observed patterns or rates.

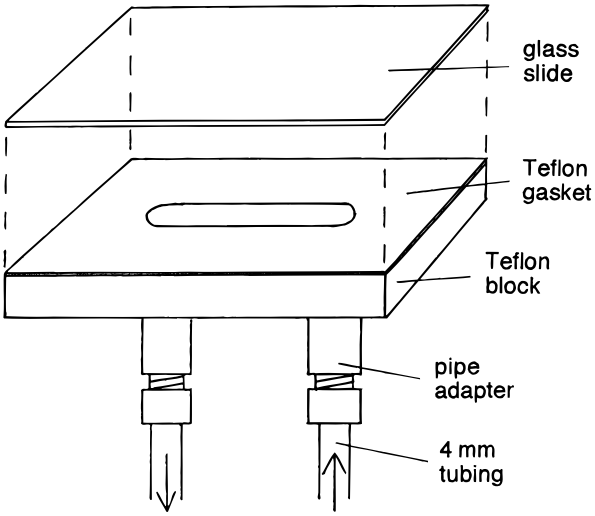


Figure 3. Schematic diagram of the Teflon reaction cell. Steel clamp is not illustrated.

Magnesium strips were cut (99.9%, Fisher, 0.17 mm thick × 3.2 mm wide), manually polished just before use with Buehler LTD Carbimet 600 grit grinding paper, and wiped with a Kimwipe. Magnesium powder (50 mesh, 99+%, Aldrich) and magnesium amalgam (2% by weight in triple-distilled mercury) were handled under argon in an Aldrich AtmosBag.

Instruments. Gas chromatograms were recorded on a Perkin-Elmer Sigma 300 gas chromatogram with a flame ionization detector. The capillary column was a Supelcowax 10 (30 m, 0.75 μm i.d.). Spectroscopic analyses were performed with a Hitachi U-2000 dual beam UV/vis spectrophotometer. Initially, an Olympus SZ60 binocular photographic microscope and PM10ADS exposure control unit were used to take photographs on Kodak Tri-X Pan or Gold Plus (ASA 400 or 200) film. Recently, equipment has been upgraded to a Nikon SMZU trinocular microscope, a JVC 1280U video camera, and a Leica Quantimet 500 MC Image Analysis System. The Leica software allows for storage of images on disk and measurement of features on screen.

Reaction Cell. The reaction cell was constructed from Teflon parts purchased from Berghof/America and is illustrated in Figure 3. A block of PTFE Teflon was cut (5 × 2.5 × 0.6 cm). Two Teflon male pipe adapters (4 mm) were threaded into the back of the block so that the center of the pipes were separated by 2.3 cm. A groove connecting the pipe adapters was milled into the block, resulting in a reaction vessel 2.3 cm long, 0.4 cm wide, and 0.25 cm deep. The magnesium strip (2.0 cm long) was placed in this groove, and a glass slide (5 × 2.5 cm) was clamped over the groove. Teflon tape served as a gasket. Approximately 20 cm of flexible Teflon tubing (4 mm in diameter) was connected to the inlet for introduction of solution. The outlet flowed through a stopcock and into a waste container.

The disassembled apparatus was dried overnight at 80 °C before use. The magnesium strip was placed in the groove, and the apparatus was assembled without tightening the clamp. It was then placed back in the oven for 5 min. The apparatus was again removed and purged with argon until introduction of the solution.

Unless noted otherwise, solutions were prepared with 20 mL of THF, 3.7 mL of bromoethane (50 mmol), and 10 mg LCV (0.026 mmol). The solution was bubbled with prepurified oxygen for about 15 s. A glass syringe and stainless steel needle were used to inject the solution through a rubber septum into the 4 mm Teflon tubing and into the reaction cell.

In a typical experiment, approximately 5 mL of solution was initially flowed through the cell to rinse and fill it. The stopcock was then shut, and observations were made under static conditions (no flow). Timing was begun as soon as

---

(28) Ashby, E. C.; Buhler, J. D.; Lopp, I. G.; Wiesemann, T. L.; Bowers, J. S., Jr.; Laemmle, J. T. *J. Am. Chem. Soc.* **1976**, *98*, 6561.

solution contacted the magnesium surface. The cell was flushed with 1 or 2 mL of fresh solution when the indicator became so dark that the surface was no longer visible (this was variable but typically occurred after 5 min). If no indicator was being used or if the reaction was occurring only very slowly, the cell was flushed at least every 10 min.

Mechanistic Studies. Reactions to be followed by product analysis were done in 50 mL, three-necked (19/22 joints) round bottom flasks. Typically 12 mmol of 4-bromotoluene and 2 mmol of iodoethane (initiator) were introduced into the flask with 20 mL of THF and 14 mmol of magnesium. This was stirred until all magnesium had reacted (10−25 min). Using a stainless steel cannula and positive argon pressure, the Grignard reagent solution was then transferred into a 100 mL flask containing 14 mmol of LCV in 20 mL of THF, and the mixture was stirred 2−5 min. One milliliter aliquots of solution were passed down a short silica column before GC analysis to remove magnesium salts. Argon was used to exclude air in some experiments, and air or prepurified oxygen was deliberately introduced in others.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. This material is also based upon work supported by the National Science Foundation under Grant No. CHE-9405038.

JO951626O