Ultrasonic Tribochemistry: The Effect of Ultrasound on Metal Powders

Stephen J. Doktycz

Final Seminar

December 11, 1989

The use of high intensity ultrasound to enhance the reactivity of metal surfaces has become a routine synthetic technique [1]. In spite of a large number of recent descriptive reports [2], the origin of heterogeneous sonochemical rate enhancements in both stoichiometric and catalytic reactions remains largely unexplored. In comparison, a detailed understanding of the mechanism of homogeneous sonochemistry has recently been developed [3]. Knowledge about the reaction conditions created by ultrasonic irradiation of liquid-solid interfaces, however, is much more limited [1,2j].

When a liquid is subjected to high intensity ultrasound, acoustic cavitation (i.e., the formation, growth, and implosive collapse of bubbles in a liquid [1]) occurs. If cavitation takes place in a homogeneous liquid, intense local heating results and shockwaves are produced. If it occurs near an extended liquid-solid surface, the collapse is extremely asymmetric and generates a high-speed jet of liquid directed at the surface [4]. The impingement of this jet and related shockwaves can create localized erosion (which produces highly reactive surfaces) [4,5], improve mass transport [1], and cause particle fragmentation (which increases the surface area of friable solids [6]).

The relative contributions of each of these physical mechanisms to the increase in heterogeneous reactivity is not known. In addition, these investigations of cavitation at bulk liquid-solid interfaces may not be relevant to the powders generally used in chemical reactions. The physical mechanisms responsible for the activation of metal *powders* by ultrasound must be, at least in part, quite different. Microjet formation, for example, requires an extended surface [7]. At 20 kHz, bubble diameters before collapse are  $\approx 200 \ \mu m$ . With powders this size or smaller, bubble deformation during cavitation will not occur.

To understand more fully the origins of heterogeneous sonochemistry, the effects of ultrasonic irradiation on chemical reactivity, particle and surface morphology, and atomic surface composition of Cu and Zn powders have been examined. The Ullman coupling reaction (eq. 1) (for copper) and the Reformatsky reaction (eq. 2) (for zinc) have been used as mechanistic probes of the chemical effects of ultrasound. In addition, a series of transition metals (Cr, Mo, and W) have been used as probes of the conditions present during irradiation of metal powder slurries.

The effects of ultrasound on the reactivity of Cu metal as a stoichiometric reagent have been documented in the literature in two cases: the Ullman coupling [8] (where  $C_6H_4$  (NO<sub>2</sub>)I is 2-iodonitrobenzene)

 $2C_{6}H_{4}(NO_{2})I + 2 Cu \rightarrow (NO_{2})H_{4}C_{6}-C_{6}H_{4}(NO_{2}) + 2 CuI$ (1)

and the reaction of Cu with salicylalaniline to form uncharacterized copper complexes [9]. In the former case, it was found that ultrasonic pretreatment of the copper (flakes,  $\approx 90 \ \mu m$  diameter and <1  $\mu m$  thickness) increased the rate of coupling up to 64-fold over the thermal reaction [8]. To determine the effect of ultrasound on the reactivity of copper powder, a slurry of copper powder was irradiated *in the absence of substrate* (2iodonitrobenzene) and then the rate of coupling measured upon addition of substrate. Ultrasonic irradiation of 75  $\mu m$  average diameter Cu powder substantially increases its reactivity ( $\geq$ 50-fold) in the Ullman coupling reaction. The effectiveness of ultrasonic pretreatment demonstrates that ultrasound produces an irreversible change in the Cu powder. Auger electron spectroscopy depth profiles of the Cu powder before and after irradiation indicate that before sonication there is a thick and complete oxide (Cu<sub>2</sub>O) coating which is completely removed after 4 h irradiation. Accompanied by the loss of surface oxide are dramatic changes in surface morphology of the Cu powder. Scanning electron micrographs of the powder before and after irradiation show that extensive surface roughening occurs with sonication.

The effects of ultrasound on 5  $\mu$ m average diameter Zn powder are equally significant. Ultrasonic pretreatment of the Zn powder increases its reactivity in the Reformatsky reaction >50-fold.

$$RR'C=0 + Zn + BrCH_2CO_2R'' \rightarrow RR'C(OH)CH_2CO_2R''$$
(2)

Elemental depth profiles using sputtered neutral mass spectrometry [10] were obtained on the Zn powder before and after ultrasonic irradiation. An appreciable oxide coating initially present on the Zn powder is significantly reduced after irradiation. In addition, extensive changes in surface morphology and individual particle morphology occurs with sonication. The Zn particles initially are extremely smooth and spherical, but upon irradiation the surface is noticeably roughened. Simultaneously, particle agglomeration forms ~50 µm aggregates after 30 min of irradiation.

We believe that the observed changes in reactivity, particle and surface morphology, and surface composition of the powders are due to high velocity interparticle collisions [2j,11]. Ultrasonic irradiation of liquidsolid slurries creates shockwaves and turbulent flow which produce such collisions. If particles collide head-on, they can do so with enough energy to cause localized melting at the point of contact. This results in particle aggregation and the exposure of highly reactive metal surfaces. If particles collide at a glancing angle, increased surface roughness and cracking of the oxide layer can result. The sonochemical activation of Zn and Cu powders comes primarily from loss of oxide passivation.

In order to better understand the conditions present when metal particles collide, a series of transition metals has been used to probe the maximum temperatures and velocities reached during interparticle collisions. Chromium (m.p. 1857°C), molybdenum (m.p. 2617°C), and tungsten (m.p. 3410°C) were irradiated as slurries in decane; scanning electron micrographs were taken before and after irradiation. The results for =10  $\mu$ m average diameter powders show that substantial surface alteration and agglomeration occurs for Cr and Mo. In striking contrast to Zn, Cu, Cr, and Mo powders, ultrasonic irradiation of W powder produces no appreciable effects. It can therefore be concluded that the peak temperatures reached during interparticle collisions must fall roughly between 2600°C and 3400°C, for particles of =10  $\mu$ m diameter.

Particle velocity estimates at impact were also made by determining volumes of interparticle necks by SEM. If full melting of the neck region is assumed to occur during collision then the energy of collision can be calculated from heat capacities and heats of fusion applied to the volumes of interparticle necks. Repeating this calculation for Zn-Zn, Cr-Cr, and Sn-Fe interparticle collisions results in an estimate of the velocity at impact ranging from 100 m/s to 500 m/s, for particles of  $\approx 10 \,\mu\text{m}$  diameter.

## References

- (a) Ultrasound: Its Chemical, Physical, and Biological Effects; 1 Suslick, K. S., Ed.; VCH Publishers: New York, 1988. (b) Suslick, K. S. Modern Synthetic Methods 1986, 4, 1. (c) Suslick, K. S. Adv. Organometallic Chem. 1986, 25, 73. (d) Lindley, J.; Mason, T. J. Chem. Soc. Rev. 1987, 16, 275. (a) Boudjouk, P. Ultrasound: Its Chemical, Physical, and Biological 2. Effects; Suslick, K. S., Ed.; VCH Publishers: New York, 1988. (b) Lindley, J.; Mason, T. J. Chem. Soc. Rev. 1987, 16, 275. (c) Luche, J. L.; Damiano, J. C. J. Am. Chem. Soc. 1980, 102, 7926.
  (d) Petrier, C.; Gemal, A. L.; Luche, J. L. Tetrahedron Lett. 1982, 23, 3361. (e) Luche, J. L.; Petrier, C.; Gemal, A. L.; Zikra, N. J. Org. Chem. 1982, 47, 3805. (f) Luche, J. L.; Petrier, C.; Lansard, J. P.; Greene, E. A. J. Org. Chem. 1983, 48, 3837. (g) Petrier, C.; Luche, J. L.; Dupuy, C. Tetrahedron Lett. 1984, 25, 3463. (h) Boudjouk, P.; Han, B. H. Tetrahedron Lett. 1981, 22, 3813. (i) Han, B. H.; Boudjouk, P. Tetrahedron Lett. 1981, 22, 2757. (j) Suslick, K. S.; Casadonte, D. J. J. Am. Chem. Soc. 1987, 109, 3459. (k) Einhorn, C.; Allavena, C.; Luche, J. L. J. Chem. Soc., Chem. Commun. 1988, 5, 333. (1) Einhorn, J.; Einhorn, C.; Luche, J. L. Tetrahedron Lett. 1988, 5, 333. Suslick, K. S.; Schubert, P. F. J. Am. Chem. Soc. 1983, 105, 3. (a) 6042. (b) Suslick, K. S.; Flint, E. B. Nature 1987, 330, 553. (c) Suslick, K. S.; Cline, Jr., R. E.; Hammerton, D. A. J. Am. Chem. Soc. 1986, 108, 5641. (d) Suslick, K. S.; Schubert, P. F.; Goodale, J. W. IEEE Ultrason. Symp. Proc. 1981, 612. (e) Doktycz, S. J.; Suslick, K. S. J. Am. Chem. Soc. 1990, in submission. 4. (a) Benjamin, T. B. Phil. Trans. A 1966, 260, 221. (b) Lauterborn, W.; Hentschel, W. Ultrasonics 1985, 24, 59. (c) Preece, C. M.; Hansson, I. L. Advan. Mech. Phys. Surfaces 1981, 1, 199. de Souza-Baroza, J. C.; Petrier, C.; Luche, J. L. J. Org. Chem. 5. 1988, 53, 1212. (a) Suslick, K. S.; Casadonte, D. J.; Green, M. L. H.; Thompson, M. 6. E. Ultrasonics 1987, 25, 56. Suslick, K. S.; Green, M. L. H.; Thompson, M. E.; Chatakondu, K. (b) J. Chem. Soc., Chem. Commun. 1987, 900. 7. (a) Plesset, M. S.; Chapman, R. B. J. Fluid Mech. 1971, 47, 283. (b) Neppiras, E. A. Physics Reports 1980, 61, 159 and references therein.
- 8. Lindley, J.; Mason, T. J.; Lorimer, J. P. Ultrasonics 1987, 58, 542.

- Kuzharov, A. S.; Vlasenko, L. A.; Suchkov, V. V. Zh. Fiz. Khim. 1984, 58, 542.
- 10. (a) Oechsner, H. Thin Film and Depth Profiling Analysis; Oechsner, H., Ed.; Springer: New York, 1983.
  - (b) Reuter, W. SIMS V; Benninghoven, A.; Colton, R. J.; Simmons, S.; Werner, H. W., Eds.; Springer: New York, 1986; pp. 44, 94.
- 11. (a) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. Solid State Ionics 1989, 32/33, 444.
  - (b) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. Chem. Materials 1989, 1(1), 6.
  - (c) Suslick, K. S.; Doktycz, S. J. J. Am. Chem. Soc. 1989, 111, 2342.
  - (d) Doktycz, S. J.; Suslick, K. S. Science, submitted for publication.
  - (e) Suslick, K. S.; Doktycz, S. J. In Advances in Sonochemistry; Mason, T. J., Ed.; JAI Press: London, 1989, vol. 1.