

유기 초음파화학 · 초음파를 이용한 올레핀의 수소화 반응

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Organic Sonochemistry · Ultrasonically Promoted Hydrogenation of Olefin

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Ultrasound facilitates a wide variety of organic reactions, particularly heterogeneous reactions.¹ Reactions in which metals function as catalytic as well as stoichiometric agents have been ultrasonically promoted, leading, in general, to higher yields of product(s) in shorter reaction times under milder conditions than when conventional conditions are employed. Catalytic hydrogenation of olefins under the influence of high intensity ultrasound has also been investigated but under conditions rarely used in the laboratory. For example, Moulton and coworkers, using elemental nickel or copper chromite catalysts and hydrogen at high pressures and temperatures in a flow system obtained good yields of the saturated products from soybean oil with one hundred fold rate acceleration using ultrasonic waves.² Marinisco claimed that the autoclave normally required for the hydrogenation of shale, lignite, coal, peat and petroleum residues could be replaced by very high frequency (1~3 Mc) ultrasonic equipment.³ Saracco successfully hydrogenated olive oil over Raney nickel using ultrasonic waves at 500~1000 KHz.⁴ We reported that low frequency (50 KHz) ultrasound from a common laboratory ultrasonic cleaner accelerated the hydrogenation of olefins using palladium on carbon and formic acid as the source of hydrogen.⁵ We have extended our studies and report here the beneficial effects of ultrasonic wa-

ves in palladium catalyzed hydrogenation using hydrogen gas in a simple apparatus.

EXPERIMENTAL SECTION

The palladium catalyst (1% Pd on activated carbon) was used as obtained from Aldrich. Absolute ethanol was used from stock without further purification. The reagents listed in the table were obtained commercially and used as purchased only if >97% pure as determined by NMR and GLC. When needed the reagents were purified by distillation or crystallization to at least 97% purity. Heat Systems-Ultrasonics INC, Model W-800 Probe Sonicator (20 KHz, 117 V, 800 Watt capacity, operated at 30% output power) was used for these experiments(sonic reactor; see Fig. 1).

NMR spectra were obtained on a Bruker AC 80 spectrometer with tetramethylsilane as an internal reference. Infrared spectra were taken on a Jasco-A-1 model. Product analyses were carried out on a Varian 3300 instrument equipped with a FID detector and a stainless steel column packed with 10% OV-101, chromosob W HP 80/100 (2 m × 1/8 in) and a linear temperature programmer. Peak areas were calculated from the analog integration trace of a Varian 4290 GC terminal recorder equipped with a thermographic integrator.

Typical Experiment: Hydrogenation of *t*-stilbene was illustrated. A dry nitrogen-filled probe reac-

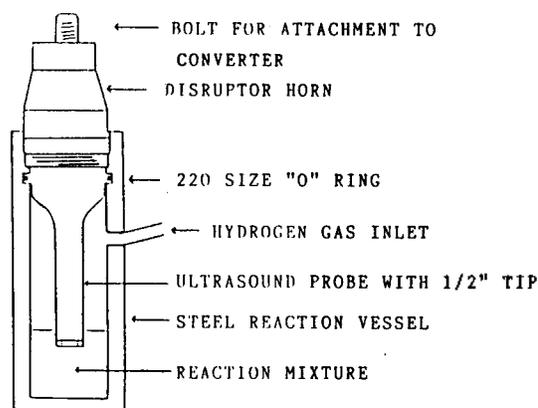


Fig. 1. Schematic diagram of the apparatus.

tor was charged with *t*-stilbene (1.8 g, 0.01 mmol), 1% palladium on carbon (0.25 g, 1.17×10^{-3}), absolute ethanol (10 mL) and benzene (10 mL). The ultrasonic probe was placed in contact with reaction solution. The reactor (Fig. 1) was cooled with ice (inside temperature of reaction mixture was raised to 35 °C during sonication due to heat generation), flushed and pressurized with hydrogen (30 psi). After sonication for 1 hr, the probe and hydrogen gas connecting line were removed and the contents were filtered. The solid was washed with methylene chloride, filtered and the combined filtrates were concentrated on a rotary evaporator. The residual solid was recrystallized (ethanol-pentane) to give 1.73 g (95% yield) of bibenzyl, mp 51–52 °C (lit.⁶ 52.2).

RESULTS AND DISCUSSION

We found that hydrogen, catalyzed by palladium, reacts essentially quantitatively with a variety of olefins in one hour at 35 °C and 30 psi (about 2 atmospheres pressure) using an ultrasonic probe. Our results are summarized in the Table 1. In the absence of ultrasonic waves, hydrogenation proceeded at a greatly reduced rate. For example, at 0 °C and 30 psi of hydrogen, styrene gave only 8% of ethylbenzene, and *t*-cinnamaldehyde did not react. Upon raising the temperature to 30, *t*-cinnamaldehyde gave only a 33% yield of 3-phenylpropanal. In addition to the high yields, this technique has the added attraction of being mild enough to

Table 1. Ultrasonically accelerated hydrogenation of olefins

Olefin	Product	Yield (%, isolated)
1. $C_7H_{15}CH=CH_2$	$n-C_9H_{20}$	95
2. $PhC \equiv CH$	$PhCH_2CH_3$	96 ^b , 56 ^c
3. $n-BuOCH=CH_2$	$n-BuOCH_2CH_3$	95
4. $PhCH=CH_2$	$PhCH_2CH_3$	96
5. $PhC=CH_2$	$PhCH(CH_3)_2$	98
6. <i>t</i> - $PhCH=CHCN$	$PhCH_2CH_2CN$	95
7. <i>t</i> - $PhCH=CHCOCH_3$	$PhCH_2CH_2COCH_3$	96
8. <i>t</i> - $PhCH=CHCOOCH_3$	$PhCH_2CH_2COOCH_3$	96
9. <i>t</i> - $PhCH=CHPh$	$PhCH_2CH_2Ph$	95
10. <i>t</i> - $PhCH=CHCHO$	$PhCH_2CH_2CHO$	94
11. Indene	Indane	93
12. 2-Cyclohexen-1-one	Cyclohexanone	93
13. Acenaphthylene	Acenaphthene	94 ^d
14. Methyl oleate	Methylstearate	97

^aTypical reactions were sonicated with probe at 35 °C for one hour using 1 : 1.17×10^{-3} mole ratio of olefin: Pd under 30 psi hydrogen pressure. ^bReaction vessel (see; Fig. 1 at experimental section) was not cooled with ice. ^cHydrogen pressure 80 psi. Styrene was formed in 44% yield by NMR as a partial hydrogenation product. Phynylacetylene was not detected by NMR and GC. ^d10 mL of benzene used to dissolve olefin.

permit the use of a variety of functional groups. Thus nitriles, esters, ketones and aldehydes are unaffected. In contrast to our earlier synthetic efforts using ultrasonic waves in which we used a common laboratory ultrasonic cleaner, the work reported here required the greater intensity of the immersion horn. We used a Heat Systems Probe Sonicator with a fitted steel reaction vessel as shown in the Fig. 1. This configuration was convenient for control of reaction temperature and pressure. Immersion of the vessel in a suitable bath provided temperature control. Pressure was monitored by a gauge attached to the side arm. While most of the reactions were run at 35 °C and 30 psi we did examine, briefly, the effects of varying pressure as shown in the Fig. 2.

We found, for example, that increasing the hyd-

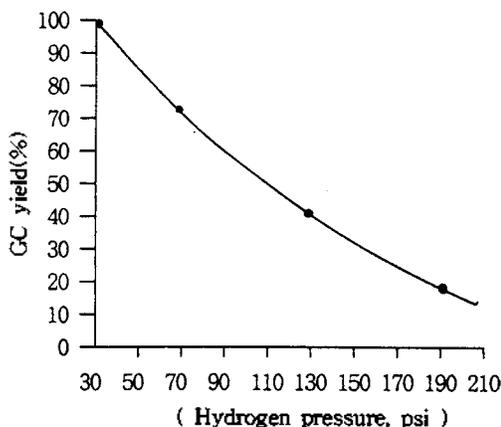


Fig. 2. Ultrasonic induced hydrogenation of α -methylstyrene with Pd/H₂ at 35 °C for 1 hr on various hydrogen pressure.

rogen pressure from 30 to 70 psi decreased the yield of cumene from α -methylstyrene from 98% to 72%. Increasing the pressure to 130 psi reduced the yield of cumene to 43%. Also, when the same reaction was carried out at 190 psi, α -methylstyrene was reduced to cumene in only 22%. Rate accelerations of chemical reactions attributed to ultrasonic irradiation arise from energy released by the collapse of partially evacuated bubbles or cavities formed in the liquid by the low pressure region of an ultrasonic wave.⁷ The energy available from this process, cavitation, is considerable leading to temperatures of 2000~3000°K and pressures of approximately one thousand atmospheres for periods of approximately 10⁻²⁶ seconds.⁸ These conditions are severe enough to clean metal surfaces and to fracture friable solids. Both processes would increase the activity of supported catalysts. We attribute the increased rate of hydrogenation to these effects. The decrease in the rate of hydrogenation when the hydrogen pressure is increased parallels a similar observation made by Moulton² and is probably the result of that increased pressure causing a suppression of cavity formation in the reaction medium.

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