A Simple and Inexpensive Alternative to a Medium-Pressure Hydrogenation Shaker-Type Apparatus

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Abstract: Materials and directions for the assembly of a safe and low-cost medium-pressure hydrogenator are provided. Most items required for the construction of this apparatus were readily available at local home improvement stores. The apparatus was tested at a pressure of 60 psi, and typical experiments were performed at 60 psi.

Introduction

Recently, this laboratory had the need to perform medium-pressure catalytic hydrogenations at ambient temperature, but did not have the resources to purchase a costly commercial shaker-type apparatus. To meet this need, a new and cost effective (total cost ca. $30.00) bottle-containment system was designed to be used in conjunction with the Parr 250-mL borosilicate-glass bottle, a hydrogen-gas cylinder, and a hydrogen-gas regulator. Shown below is a schematic (Figure 1) and a photographic (Figure 2) representation of the reaction-vessel-containment system designed in this laboratory. It should be noted that this bottle-containment system was used routinely at pressures of 60 psi without leaks or stress upon this system. (Note: All pressure tests were conducted over a 30 min period using an inert gas, nitrogen, prior to using hydrogen gas in this system.)

Preliminary Remarks

The hydrogenation apparatus presented herein has been used in an undergraduate research setting by well-trained undergraduate research students (usually at the junior or senior levels), *with proper faculty supervision*. It is essential that the supervising faculty member be knowledgeable about and experienced in performing catalytic hydrogenations [1]. Moreover, the supervising faculty member should be conversant in working with compressed gasses [2], particularly hydrogen gas [3].

Safety. It is important that proper precautions are taken while employing this apparatus. This apparatus should be used in a well-ventilated area. No flames or other possible ignition sources should be used while working with hydrogen gas, as it is very explosive. In addition, to further reduce explosion risk, care should be exercised to prevent the exposure of hydrogen gas to any incompatible oxidants (consult an MSDS form for additional details).

All persons working with this equipment should wear appropriate eye protection (goggles). In addition, it is also suggested that all connections in this apparatus be tested for leaks (a soapy water solution works well) using an inert gas, such as nitrogen, prior to use. Moreover, the maximum suggested pressure for these borosilicate-glass bottles, as suggested by Parr, is 60 psig; thus, the maximum pressure for leak tests and reactions should not exceed these manufacturer's recommendations. Finally, it is strongly advised that the entire reaction-vessel-containment system be enclosed behind a safety shield for additional protection.

For sample preparation, all reaction mixtures should be degassed prior to use. This is most efficiently accomplished using one of the following two methods: (1) Bubble a stream of nitrogen gas through the solution for approximately fifteen minutes prior to attaching the borosilicate-glass bottle, see below, to the containment system or (2) Evacuate the flask containing the reaction mixture and subsequently refill the flask with an inert gas, such as argon or nitrogen. Repeating this procedure three times should minimize any exposure of the reaction mixture to oxygen.

Construction Procedure

The bottom assembly is fashioned as follows. Each threaded zinc rod is fitted with one 1/4-in nylon locking hex nut. The four rods are inserted through the equidistant holes of the 1-in floor flange [4] such that the flat surface of the flange faces upwards and the lock nuts rest against its contoured surface. The threaded rods are then fixed into place against the floor flange using 1/4-in SAE washers and a regular 1/4-in hex nut.

The taped borosilicate bottle, containing the reaction mixture and a magnetic stir bar, is placed against the flat portion of the first floor flange inside of the four upright treaded rods, and this partial assembly is placed on top of a magnetic stirrer.

The upper portion of this assembly is then prepared as follows. A 1-in bushing is screwed into the central hole of the contoured face of the second floor flange. The copper tubing (1/4-in) is inserted into the central hole of the flange/bushing assembly and a number 6 rubber stopper is affixed to this tubing such that the stopper rests next to the bushing with the tapered portion of the stopper facing away from the bushing.

The stopper is fitted into the neck of the bottle and the upper portion of this assembly is placed against the stopper, such that the threaded rods pass through the four equidistant holes of this plate. Each rod is then fitted with a second SAE washer

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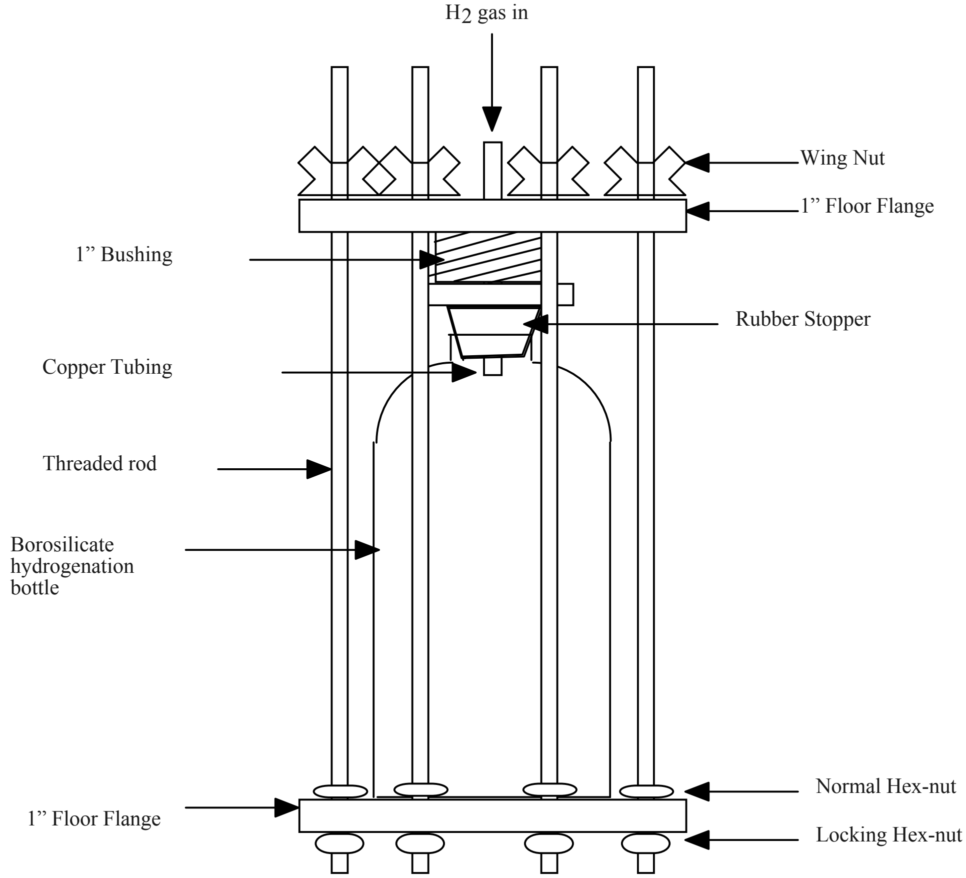
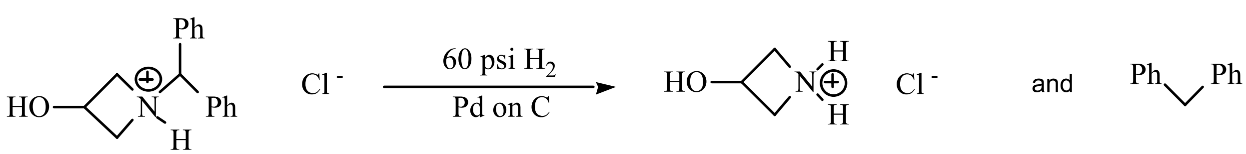


Figure 1. Schematic representation of reaction-vessel-containment system.



1 **2**

and the entire upper assembly is very tightly secured against the rubber stopper using ¼-in wing nuts.

Finally, the entire cage is covered with carpenter’s cloth, a heavy gauge steel mesh, which is held in place using cable ties. For additional safety, the entire bottle-containment system is surrounded with a safety shield.

The second stage of a hydrogen gas regulator is used to deliver the required pressure to the reaction vessel. The regulator itself is connected to a three-way brass "T" joint using copper tubing. This same T joint is also attached to the other end of the copper tubing fitted with the number 6 rubber stopper. The third terminus of the T joint is connected to a needle valve and the entire system can be readily vented to a well-ventilated area through means of this valve (Figure 3).

Although a magnetic stir bar and a stir plate are used for the agitation required for this reaction in place of a shaker-type apparatus, it was found that reactions took place in a satisfactory amount of time. Because we do not have a commercial Parr apparatus available, comparative kinetic studies of standard Parr equipment versus this inexpensive model have not been performed. One of the authors prior experience, however, is that hydrogenation with the inexpensive equipment can actually proceed faster than with commercial Parr equipment, because hydrogen entrainment from cavitation of a rapidly spinning stir bar can effect more efficient movement of hydrogen into the reaction solution than can horizontal, vigorous shaking. Nevertheless, the actual rate is strongly dependent on size and shape of the spin bar and its rate of spin, something that we have not made an effort to hold constant and quantitate.

A Typical Reaction Procedure

The above reaction is carried out according to the procedure reported by Triggle [5]. Accordingly, 0.23 g of 5% Pd/C, 2.33 g (9.74 mmol) of the hydrochloride salt **1**, 25 mL of ethanol, and a magnetic stir bar are placed in a 250-mL borosilicate-glass bottle, and the resulting mixture is degassed by placing the sample under vacuum, followed by purging with anhydrous nitrogen gas. This flush and fill procedure is repeated three times in order to ensure satisfactory removal of dissolved oxygen. Subsequently, the reaction vessel is placed inside of the apparatus and secured using the wing nuts, carpenter’s cloth and a safety shield; see above. The reaction

Figure 2. Photograph of reaction vessel containment system.

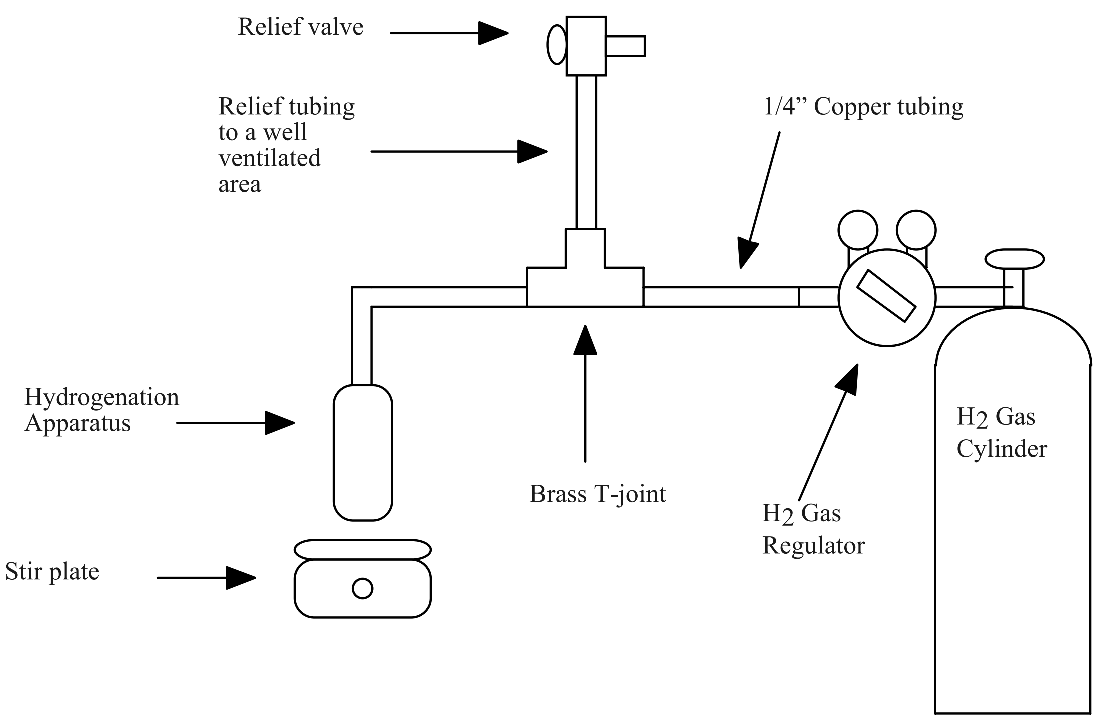


Figure 3. Diagram of the hydrogen-gas delivery system.

mixture is subjected to 60 psi of H_2 and stirred vigorously for 72 h. After this time interval, the pressure in the system is released into a fume hood and the sample evacuated and purged with N_2 in order to remove any residual hydrogen gas. The catalyst is removed by filtration and the solvent is removed under reduced pressure. The resulting mixture is redissolved in 50 mL of methanol and extracted three times with 25 mL of hexane. The resulting methanol solution is concentrated in vacuo to afford 0.95 g (8.6 mmol) of the ammonium salt **2** in 61% yield. This material gives physical and spectral characteristics identical to those reported previously [4].

Conclusion

This containment system, used in conjunction with a magnetic stir plate, was capable of withstanding pressures of 60 psi for prolonged periods of time. The parts used in the assembly of this reaction-vessel-containment system were conveniently found at most home improvement stores and were relatively inexpensive (total cost, ca. $30.00). This reaction-vessel-containment system has been used safely and routinely in this laboratory for carrying out medium-pressure catalytic hydrogenations at ambient temperature. Again, it is strongly advised that the individuals employing this apparatus be experienced in performing catalytic hydrogenations and knowledgeable in the use of compressed gases and medium-pressure devices.

Itemized List of Parts

1/4-in copper tubing
1/4-in brass three-way "T" joint with gas-tight fittings
1/4-in brass needle valve with gas tight fittings
hydrogen-gas regulator with gas-tight fittings for 1/4-in copper tubing
4 threaded rods, 1-ft length and 1/4-in diameter with standard 20-gauge threading
2 1-in Floor Flanges
1-in bushing
4 1/4-in hex nuts
4 1/4-in nylon lock nuts
8 1/4-in SAE washers
1-ft by 2-ft section of carpenters cloth
2 or 3 14-in cable ties
250-mL borosilicate-glass reaction bottle obtained from Parr

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References and Notes

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3. Braker, W.; Mossman, A. L. *Gas Data Book, 6th Ed.*; Matheson Gas Products: Secaucus, NJ, 1980; pp 366–369.
4. The floor flange is the name of a plumbing item, and it is referred to by this name in home improvement stores. They are predrilled and can be used without any modification.
5. Chatterjee, S. S.; Triggle, D. J. *Chem. Commun.* **1968,** 93.