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A Balloon Filled with Nitrogen Gas Does Not Satisfy the Air- or Moisture-Free Reaction Condition

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In the basic reaction media using Grignard reagents, alkyllithum, metal hydrides and organometallic reagents, water can act as a strong acid to ruin the reagents.[1] On the other hand, in the reaction using Lewis acids such as thionyl halide, phosphorous halide, boron halides, or organoaluminium compounds, water can act as a nucleophile that damages those reagents. Due to these harmful properties of water, synthetic researchers have focused extensive attention on technical methods to retain an anhydrous or air-free condition. Although the Schlenk technique[2] and glove box[3,4] can be used to accomplish such conditions precisely and perfectly, tedious installation and careful utilization processes are required. Therefore, the convenient and easier method of using a rubber balloon filled with nitrogen gas has been considered and used to maintain an anhydrous condition for air-sensitive reactions.[5,6]

In general, a balloon filled with inert gas connected to the reaction flask excludes the outer atmosphere from the reactor due to the higher inside pressure than that outside the reactor. Helium gas in a balloon is, however, reported to be exchanged with the external humidity due to gas permeation.[7] We wondered whether a reactor could be protected only by a balloon filled with inert gas to the extent of satisfying the anhydrous condition. To confirm the possibility, we analyzed the gases in a nitrogen gas-filled balloon in a laboratory. The moisture content in the reactor connected with the nitrogen gas-filled balloon was analyzed by an IR spectrophotometer. The aim of this study was to alert researchers using a nitrogen gas-filled balloon to satisfy the anhydrous reaction condition, of the danger of outside moisture permeating very rapidly into the nitrogen gas balloon.

A schematic of the experimental setup is shown in Figure 1. The gas in the balloon was analyzed by an IR spectrometer for 60 minutes, as shown in Figure 2. In the IR analysis of the air, the absorption bands of H_2O appeared in the ranges of 3560 ~ 3928 and 1351 ~ 1905 cm^{-1} and that of CO_2 in the range of 2371 ~ 2307 cm^{-1}. The nitrogen gas (purity > 99.999%) used to fill the balloon did not show any trace of H_2O or CO_2, in complete contrast to the air in the IR analysis, as shown in Figure 2 (a). As depicted in Figure 2 (b-f), the absorption intensities of both H_2O and CO_2 increased with time. To determine the relative increases of H_2O and CO_2 contents in the

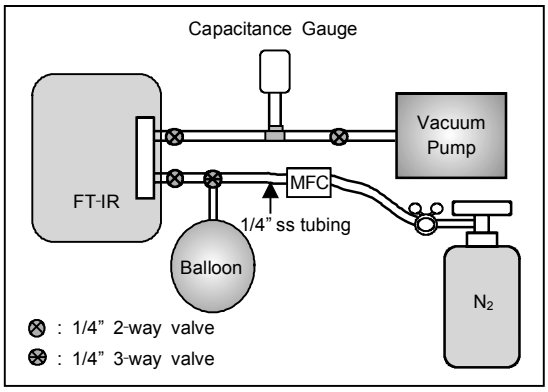


Figure 1. Schematic diagram of the apparatus for analyzing the gas content in the nitrogen gas-filled balloon using an FT-IR spectrometer (MFC: Mass flow controller).

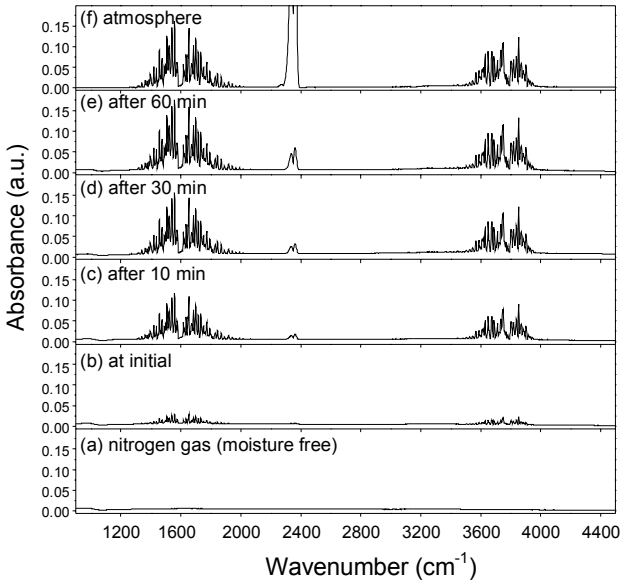


Figure 2. FT-IR spectra of the N_2 gas used to fill the balloon (a), the gas inside the balloon at the time after inflation (b), and after 10 min (c), 30 min (d), and 60 min (e). The absorption bands for H_2O appeared in the range of 3560 - 3928 and 1351 - 1905 cm^{-1}, and those for CO_2 in the range of 2307 - 2371 cm^{-1}.

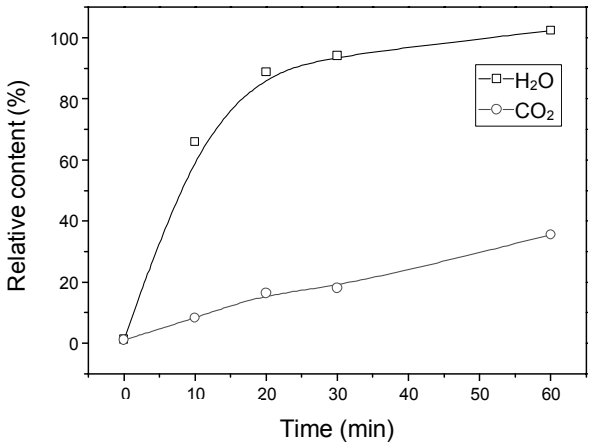


Figure 3. Relative H_2O and CO_2 contents in the balloon according to time. The relative gas contents were calculated based on the integration of IR absorption peaks at 1351 - 1905 cm^{-1} for H_2O and 2307 - 2371 cm^{-1} for CO_2.

Table 1. Calculations of FT-IR peak areas of H_2O and CO_2 in the N_2 gas used to fill the ballon, in the balloon at various time intervals, and in the atmosphere.

Gas	Time (min)	Band region (cm^{-1})		
		3560 - 3928 (H_2O)	1351 - 1905 (H_2O)	2307 - 2371 (CO_2)
N_2	-	0.054	0.0022	0.00078
In balloon	0	1.29	2.52	0.0197
In balloon	10	6.38	11.63	0.154
In balloon	20	8.59	15.68	0.306
In balloon	30	9.11	16.62	0.386
In balloon	60	9.88	18.07	0.662
Atmosphere	-	9.75	17.65	1.864

balloon, the moisture quantities in the balloon are shown in Figure 3 based on the integration of the absorption peaks in the region of 1351 ~ 1905 cm^{-1} corresponding to the symmetric bending normal mode of H_2O and compared with the atmospheric moisture content. The CO_2 content in the balloon was also obtained from the integration of the absorption peaks in the range of 2307 ~ 2371 cm^{-1}. As shown in Figure 3, the water content in the balloon increased rapidly to 14% of atmospheric water concentration even immediately after inflating the balloon with nitrogen. The water concentration in the balloon reached 65% of atmospheric water concentration in 10 minutes and almost reached equilibrium with the atmosphere after 30 minutes.

However, CO_2 gas permeated into the balloon more slowly than water, which was attributed to its affinity to the rubber surface and heavier molecular weight according to Graham's law.[8] The theoretical permeation rate of CO_2 was estimated as about 1.5 times slower than that of H_2O. Grignard reagents can react with CO_2 to be converted into the corresponding carboxylic acids. For prolonged Grignard reactions, therefore, diffusion of CO_2 into a balloon was quite noticeable and could affect the reaction because the CO_2 content was increased to 35% of the atmospheric CO_2 after 60 minutes.

In summary, analysis of the gas in a nitrogen gas-filled balloon indicated that the penetration of water molecules into the balloon achieved a moisture content of 65% of atmospheric water concentration in 10 minutes. The results presented here should alert synthetic chemists in organic or inorganic laboratories to the inability of an inert gas-filled balloon to provide a moisture-free or air-free condition in the reaction system.

Experimental Section

Thick-wall rubber balloons were purchased from Aldrich Chemical Co. The balloon was tied by a rubber band at a part of a three-way valve leading to the inlet port of an FT-IR spectrometer. The balloon was inflated and deflated five times with high purity N_2 (99.999%, Deokyang Energen Co., Korea) to remove the moisture physically adsorbed inside the balloon. The moisture content remaining in the balloon filled with a constant pressure of nitrogen (*ca*. l.5 liter) was analyzed by a BRUKER IFS 120 HR FT-IR spectrometer after inflation at atmospheric pressure. A sample holder of a stainless steel IR cell equipped with a KBr window was used. The data were recorded by accumulating 30 scans with a resolution of 4 cm^{-1} under a constant temperature of 20 ± 1 °C. A capacitance gauge attached to the vacuum line was used to confirm the inner pressure and to check for leakage in the IR cell. Data acquisition and qualitative and quantitative analyses of the IR spectra were performed using an analysis program (OPUS NT spectroscopic software) and the peak areas of H_2O and CO_2 in the balloon were calculated as shown in Table 1.

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