CHEMISTRY LETTERS, pp.217-218, 1979. Published by the Chemical Society of Japan

SPINNING GLASS CELL FOR HIGH-PRESSURE HIGH-RESOLUTION NMR MEASUREMENTS

Hiroaki YAMADA, Kazuhiko FUJINO, Masakatsu NAKATSUKA, and Akira SERA
Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657

A simple device for a spinning high-pressure glass cell eliminated the use of a hand pump and a Bourdon gauge in performing the high-pressure high-resolution NMR. Internal rotation of a substituted triazene has been examined in a dilute solution up to 3000 bars at 35°C.

Since our first success in observing ^{1}H high-pressure high-resolution NMR (HPHR-NMR) using a commercial NMR probe,$^{1)}$ several modifications have appeared.$^{2-5)}$ However, the application of the technique have been restricted within limited experimental conditions: employment of a small diameter sample cell under non-spinning condition, etc. This paper outlines an exceedingly simple device for the HPHR-NMR performance without usual high-pressure equipments such as a hand pump and a Bourdon gauge. An outstanding advantage of the present device is that one can record spectra under the sample-spinning condition which leads to an improvement in both the resolution and the S/N ratio of NMR signals.

Figure 1 illustrates the present high-pressure glass NMR cell and the rotatable assembly. The glass cell (A), made of a usual labolatory glass tube$^{2)}$ or a Pyrex tube$^{5)}$ and etched inside with a 5% aqueous hydrogen fluoride solution, was filled with a pressure indicator (a mixture of 95 mole% of phenylacetylene and 5 mole% of cyclohexane), purified mercury, and a sample solution. The pressure indicator was frozen by immersing (A) in a liquid nitrogen bath, while an additional portion of the sample solution was sucked into (A) through an open-ended capillary [(SP) in Fig. 1-(i)] so that the volume loss caused by freezing was filled up. (SP) was sealed by a microburner and (A) was put in a safety jacket fitted by a commercial spinner rotor [Fig. 1-(ii)]. The assembly was settled in a thermally controlled NMR probe. Melting and thermal expansion of phenylacetylene sufficed to generate an inner pressure up to 3000 bars (practical upper limits were 2000-2500 bars). By controlling the extent of crystallization of phenylacetylene, one can generate a nearly desired pressure in the cell. Estimation of the inner pressure was achieved by measurement of the chemical shift of the ethynyl proton of phenylacetylene whose pressure dependence was thoroughly investigated.$^{6)}$ For this purpose, its chemical shift was measured *in situ* at an upside down position in the safety jacket.

Figure 2 shows a representative spectrum change of methyl protons of 1-(m-nitrophenyl)-3,3-dimethyltriazene [$m\text{-}NO_2\text{-}C_6H_4\text{-}N{=}N\text{-}N(CH_3)_2$] in a 5 mole% solution of dichloromethane containing 1 mole% of cyclohexane as an internal reference determined by a JEOL PS-100 spectrometer at 35°C. The cyclohexane protons showed

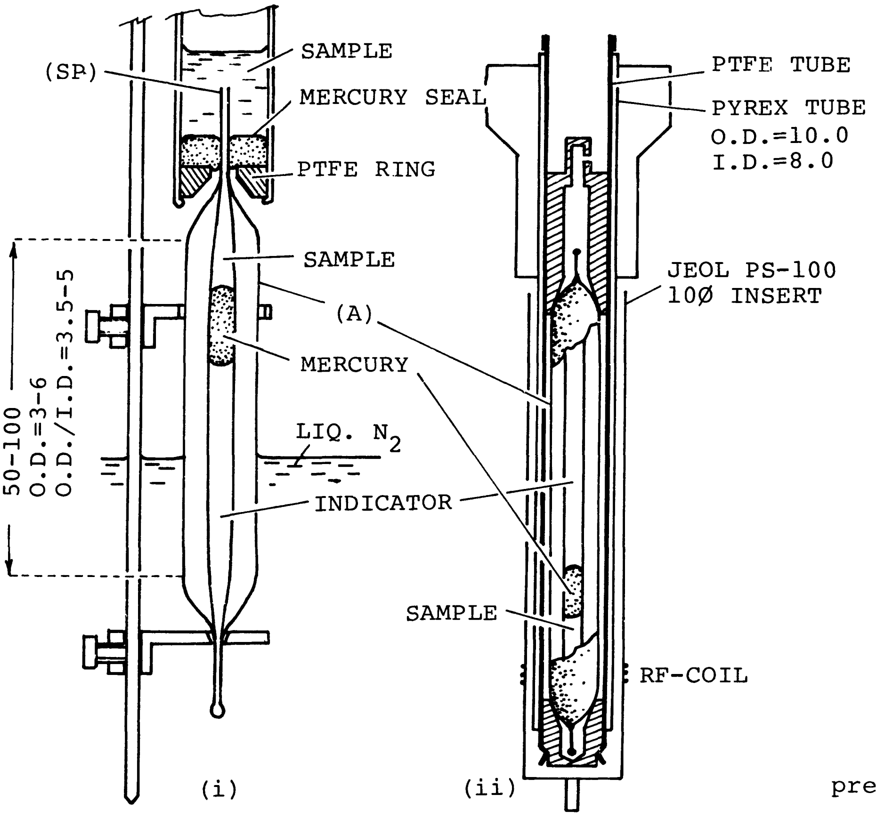

Fig. 1. (i) Set up to freeze the pressure indicator. (ii) Rotatable high-pressure assembly. Lengths are given in mm.

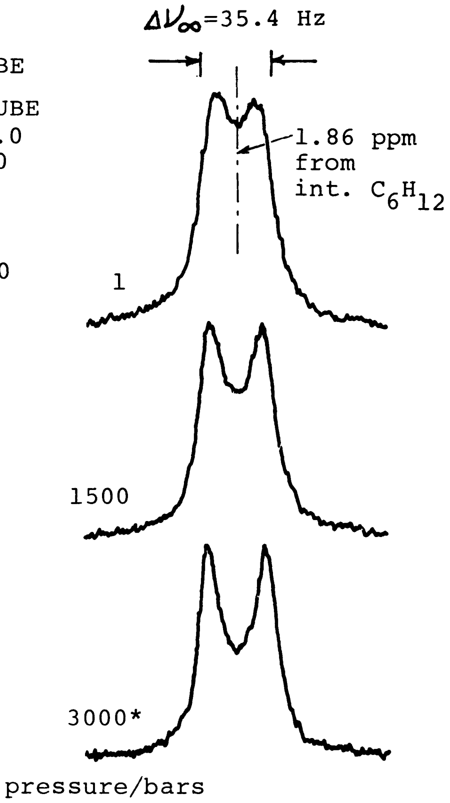

Fig. 2. Variable-pressure spectra of the N-methyl protons at 35°C. *Estimated by extrapolation from a plot of $\Delta\delta_{C\equiv CH}$ vs. P.

a good resolution of a resonance line ($\Delta\nu_{h/2}$ = 0.6 - 0.7 Hz, at ν_0 = 100MHz) with a sufficient S/N ratio, while the two methyl signals apparently became separated at high pressure. Thus the rate of rotation around the N_2-N_3 bond was slowed down with increasing pressure; that is, the rotation process was assumed to have an increase in volume at the transition state.

A detailed report on the pressure dependence of the internal rotation, along with further discussion on the pressure and temperature limitation and the safety with the present device will appear elsewhere.

References

1) H. Yamada, Chem. Lett., 747 (1972).
2) H. Yamada, Rev. Sci. Instrum., 45, 640 (1974).
3) U. Gaarz and H.-D. Lüdemann, Ber. Bunsenges. Phys. Chem., 80, 607 (1976).
4) H. Yamada, C. Itani, and K. Otsuka, J. Am. Chem. Soc., 99, 3572 (1977).
5) R. K. Williams, Rev. Sci. Instrum., 49, 591 (1978).
6) H. Yamada, S. Nishitani, K. Fujino, and A. Sera, Abstr. p-144, 16th NMR Symposium., Kyoto, November 1977.

(Received December 26, 1978)