

4705

October 27, 1981

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Subject: Structural alteration during ^{13}C CP-MAS NMR spectroscopy

Dear Professor Shapiro:

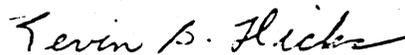
In recent studies of crystalline carbohydrates by CP-MAS ^{13}C NMR spectroscopy, we have examined α -D-glucose in its anhydrous¹ (orthorhombic) and monohydrate² (monoclinic) states. During the course of these experiments we observed that after long periods of signal averaging which were necessary to obtain spectra of glucose ($T_{1\text{H}}$ α -D-glucose $\cdot\text{H}_2\text{O}$ 77 sec, $T_{1\text{H}}$ α -D-glucose anhydrous = 40 sec), the α -D-glucose $\cdot\text{H}_2\text{O}$ was partially transformed into the anhydrous form. This phenomenon appears to depend on the duration of sample ^1H irradiation and spinning. The accompanying figure shows the progress of the α -D-glucose $\cdot\text{H}_2\text{O}$ transformation with a 256 msec acquisition time and a magic angle spinning rate of 2.1 KHz. The resonances at δ 61.77 and 64.51 represent the C-6 carbons of the monohydrate and anhydrous forms (established independently with pure compounds). An increase in the acquisition time to 0.5 sec resulted in an increase (approximately 50%), in the rate of conversion of the monohydrate. Neither ^1H irradiation (11 Gauss at 15 MHz) nor magic angle spinning (2.1 KHz) alone, for comparable periods of time, produced this structural modification. It appears that a combination of centrifugation (12-15 G of force acting on some portion of the sample) and low energy microwave irradiation (11 Gauss at 15 MHz) has a synergistic effect on the liberation of water from the crystalline state. Ultimately this water must diffuse to the walls of the rotor whereby it may escape through the vapor permeable threads of the rotor cap. Conversion seems to be limited to approximately 40% which is probably a consequence of the pressure drop across the cross section of the sample within the rotor.

So far we have only observed this effect with the monohydrate of α -D-glucose, presumably because water is known to be loosely bound to the glucose molecule³. In any event, care should be taken when examining hydrated crystals by CP-MAS NMR not to irradiate and spin the samples for unnecessarily long periods of time.

Sincerely,



Philip E. Pfeffer



Kevin B. Hicks

1. G. M. Brown, H. A. Levi, Science (1965) 1038.
2. R. C. G. Killean, W. G. Ferrier, and D. W. Young, Acta Cryst., 15 (1962) 911.
3. T. Hatakeyama, H. Yoshida, C. Nagasaki, and H. Hatakeyama, Polymer 17 (1976) 559.