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CP/MASS ^{13}C NMR Spectra of Cellulose Solids: An Explanation by the Intramolecular Hydrogen Bond Concept

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ABSTRACT: CP/MASS ^{13}C NMR spectra of wood pulp with the crystal form of cellulose I (referred to as cellulose I), cellulose regenerated from mercerized wood pulp with crystal form of cellulose II (cellulose II), and cellulose powder ground in ball mill were investigated. The spectrum of ball milled cellulose powder had broad carbon peaks at almost the same positions as those in solution, suggesting that there is no strong intramolecular hydrogen bonds of specific bond length. For cellulose I and II, one or two sharp components, in addition to broad component, were observed for each carbon and the former component was assigned to a strong intramolecular hydrogen bond. Among three possible intramolecular hydrogen bonds, O_3–H $\cdots$ O_5', O_2–H $\cdots$ O_6', and O_6–H $\cdots$ O_2', simultaneous hydrogen bonds of the former two can explain consistently all the peaks of the NMR spectrum of cellulose I experimentally observed. To explain the NMR spectrum of cellulose II, the three intramolecular hydrogen bonds are necessary.

KEY WORDS CP/MASS ^{13}C NMR / Cellulose / Cellulose I / Cellulose II / Intramolecular Hydrogen Bond /

Recently, solid state high resolution ^{13}C NMR spectra were observed, using the cross-polarization/magic angle sample spinning (CP/MASS) technique, for various cellulose samples of different crystalline form, crystallinity and super-molecular structure, revealing the usefulness of CP/MASS NMR method for analyzing the crystalline and non crystalline solid structure of celluloses.[1-9] Each peak, assigned to C_1, C_4, and C_6 carbons in anhydroglucopyranose ring, was observed to consist of one or two sharp resonance(s) and a broad one, respectively. The relative content of the sharp and broad components, estimated from integral, depended significantly on crystal structure, crystallinity and morphology.[5] In particular, the remarkable variation in the shape of the C_4 carbon peak at 80–90 ppm (tetramethylsilane was used as a reference standard) has attracted the attention of many investigators. On the basis of a linear relationship between the integrated fraction of the downfield sharp component of C_4 carbon peaks, obtained in CP/MASS ^{13}C NMR spectra and the crystallinity determined by X-ray diffraction for regenerated cellulose sample with different crystallinity and cotton, Horii *et al.*[4] concluded that the downfield sharp and upfield broad components are contributions from the crystalline and non-crystalline components, respectively. Earl and VanderHart[5] concluded from an analysis of the CP/MASS ^{13}C NMR spectra of native cellulose from several origins that the broad peaks of the C_4 and C_6 carbons are attributed to anhydroglucose on the surface of cellulose elementary fibrils in addition to non-crystalline and narrow C_4 and C_6 peaks (at 66 and 90 ppm) are due to anhydroglucose underneath the elementary

fibrils considered to be completely perfect crystalline components.

As is well known, the crystallinity of cellulose, χ_c varies significantly according to the measuring method employed. For example, cotton has $\chi_c = 73\%$ by the X-ray diffraction method, 64% by the density method and 58% by the method of water accessibility.[10] Thus, it is to no purpose to discuss the numerical coincidence of parameters (content of sharp components) evaluated from NMR resonance with χ_c estimated by other popular methods. By X-ray diffraction, the regular part in the packing between molecular chains is measured and the length should be more than 30 Å. In contrast, the ^{13}C NMR method seems almost independent of molecular chain packing, that is intermolecular interaction, but is very sensitive to the conformation of the cellobiose units of a molecular chain.

Very recently, we found that the appearance of the C_4 carbon peak of a cellulose solid over a wide range from 90—80 ppm can be reasonably explained simply by considering the intramolecular hydrogen bonds between the C_3 hydroxyl and O_5' ring oxygen, correlating the content of the broad component of C_4 carbon peak (χ_h (NMR)) with the solubility of cellulose in alkali solution.[6] A sharp component in the C_4 carbon region was found attributable to the C_4 carbon in a cellobiose unit, in which a O_3–H $\cdots$ O_5' intramolecular hydrogen bond is strongly formed and a broad component reflects the distribution of the bond strength of an incompletely destroyed intramolecular hydrogen bond.

Obviously, all references[1-9] are concerned with the peaks of only the C_4 carbon and no further study has been carried out on the theoretical analysis of the ^{13}C NMR peaks of carbons other than the C_4 carbon. This article attempts to analyze the CP/MASS NMR peaks of each carbon of various samples having the crystalline form of cellulose I or II, in view of the presence of intra- and intermolecular hydrogen bonds.

EXPERIMENTAL

Cellulose

Wood pulp cellulose (C-1) having a viscosity-average molecular weight $M_v = 2.1 \times 10^5$, a crystallinity χ_c by X-ray diffraction of 78% and the crystal form of cellulose I was used. A 100 weight part of C-1 was immersed in a 2000 weight part of 18 wt% aqueous sodium hydroxide solution at 30°C for 30 min and then hand-pressed to exclude excessive alkali from the sample. The alkalicellulose thus prepared was converted to cellulose in a 1 wt% hydrochloric acid solution and dried *in vacuo* and designated as sample code C-2, with $M_v = 1.65 \times 10^5$, $\chi_c = 55\%$ and the crystal form of cellulose II. C-1 and C-2 were ground in a ball mill at 25°C for 8 h to give cellulose powders and were designated as C-1b ($M_v = 2.0 \times 10^4$, $\chi_c = 8\%$) and C-2b ($M_v = 1.6 \times 10^4$, $\chi_c = 0\%$), respectively. Here, M_v was determined from the solution viscosity of the cadoxen solution at 25°C[11] and χ_c was evaluated by Segal's method.[12] χ_h (NMR) defined in our previous work[6] for C-1b and C-2b were 62.4 and 91.8%, respectively. These values correlated to their solubility in a 10 wt% aqueous alkali at 4°C.

CP/MASS ^{13}C NMR

CP/MASS ^{13}C NMR spectra were recorded by a JEOL FX-200 type FT-NMR spectrometer under the following operating conditions: Resonance frequency, 50.1 MHz; cross-polarization contact time, 2 ms; repetition time, 5 s; rotational velocity of magic angle sample, 3—3.5 kHz; measuring temperature, room temperature. The scan number is shown in Figure 1.

RESULTS

Figure 1 shows the CP/MASS NMR spectra of four cellulose solid samples. Table I shows the peak positions (tetramethylsilane as reference standard) and integrated peak intensity. In this table, the suffixes s and b are the

Table I. Peak assignment of cellulose samples*

Sample	Carbon position/ppm											
	C_1			C_4			C_2, C_3, C_5			C_6		
C-1	105.4			89.1	84.5[b]		75.3	72.7		65.5	63.0[b]	
	(1.00)			(0.47)	(0.53)		(1.57)	(1.51)		(0.55)	(0.38)	
C-1b	105.4	104.4[s]		90.0	83.5[b]		75.0[b]	72.9[s]		65.4	62.6	
	(1.00)			(0.29)	(0.61)		(3.16)			(0.29)	(0.55)	
C-2	107.4	105.4	102.7[s]	89.1	87.9	84.6[b]	77.0[s]	75.2	73.4[s]	63.0	62.0[s]	
	(0.19)	(0.81)		(0.13)	(0.27)	(0.60)		(3.13)		(0.88)		
C-2b	104.3[b]	97.4[b]		82.2[b]			75.5[b]			62.2[b]		
	(0.87)	(0.13)		(0.82)			(3.72)			(0.86)		
Cellulose in NaOH aq*[a]	104.7			80.0			76.4	75.0		61.9		
	(1.00)			(0.94)			(2.44)	(1.00)		(1.06)		

* Integrated intensity (in parenthesis) was normalyzed by C_1 relative intensity; b denotes a broad peak and s, the shoulder peak. *[a] Data were reproduced from ref 6.

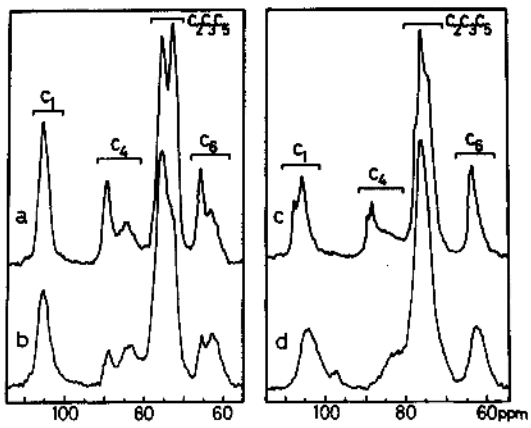

Figure 1. CP/MASS ^{13}C NMR spectra of cellulose samples: (a), C-1 (150 times scan); (b), C-1b (200 times scan); (c), C-2 (495 times scan); (d), C-2b (400 times scan).

shoulder and broad peaks, respectively. The NMR data on cellulose in aqueous sodium hydroxide solution obtained in the previous paper[6] were also included in the table for comparison. Peak assignment was carried out using the results of Voelter *et al.*[13] for β-glucose and cellobiose in D_2O for our reference. C_1, C_4, and C_6 carbon peaks were easily assignable since they were almost completely separated from each other and other carbon peaks as well. The C_2, C_3, and C_5 carbon peaks overlapped to some extent with each other in the range 77—73 ppm.

The data of Figure 1 and Table I lead to the following conclusions:

(1) For all cellulose samples except amorphous cellulose (C-2b), C_4 and C_6 carbon peaks split into one or two sharp lower magnetic field components and a broad, higher magnetic field component, respectively.

(2) The sharp components in the C_4 and C_6 carbons decrease and broad components increase by ball milling.

(3) The C_1 peak broadens by ball milling and its center position shifts to a higher magnetic field by *ca.* 1 ppm.

(4) For C-2 (cellulose having crystal form of cellulose II), the C_1 and C_4 carbon peaks each have two sharp components, but the C_1 and C_4 carbon peaks each have only one sharp component for C-1 (cellulose having crystal form of cellulose I).

(5) For C-2b (amorphous cellulose), all carbon peaks including the C_4 carbon peak contain only broad components and their peak (central) positions are near those for cellulose II dissolved in alkali solution.

(6) The C_4 carbon peak for C-2b is ob-

served at 80—84 ppm, which is slightly lower than that (80 ppm) of cellulose II dissolved in alkali, but appreciably higher than the sharp peaks (87.9, 89.1 ppm) for the C-2 sample.

(7) For the C-2, a new small peak lacking in the spectra of both the C-2 solid and cellulose dissolved in alkali, is observed at 97.4 ppm.

(1)—(3) are valid, regardless of crystal form and (1)—(4) have already been reported in the past.[1-5,7,8]

DISCUSSION

Sample C-2b has $\chi_c = 0$, $\chi_h(\mathrm{NMR}) = 91.8\%$ and is a so-called amorphous cellulose. In its CP/MASS NMR spectrum, the small peak at 97.4 ppm (experimental fact (7)) can be considered the C_1 anomeric carbon peak for cellulose oligomers formed by oxidative degradation during ball milling. Taking into consideration the experimental (5) and (6) data along with the fact that cellulose dissolved in aq. sodium hydroxide has no inter- and intramolecular hydrogen bond[6] since the C_4 carbon peak becomes singlet and sharp at 80 ppm, we can conclude that the amorphous cellulose solid contains many cellobiose units having very weak intramolecular hydrogen bonds assuming that they exist at all. The intermolecular hydrogen bond randomly formed between two or more cellobiose units may exist, but may not conspicuously influence the chemical shift of the NMR spectrum as already described. To clarify all the features of the NMR spectra for cellulose, it is adequate as a first approximation to consider the electron charge density on given carbon atoms in view of the possible presence of intramolecular hydrogen bonds, O_3–H $\cdots$ O_5'(a), O_2–H $\cdots$ O_6'(b) and O_6–H $\cdots$ O_2'(c) in cellulose solid.[14-17] If a cellobiose unit should take on the form (a) shown in Figure 2, the C_3 and C_4 carbons will occupy an ionic and cationic ends, respectively owing to the formation of a seven membered π–σ electron conjugate system. The C_1 carbon may be slightly cationized, being near the cationic end C_4 carbon. In consideration of the shielding effect induced by the electron density on the NMR spectrum, the C_1 and C_4 carbon peaks must shift towards a lower magnetic field and the C_3 carbon towards a higher magnetic field, compared to those for amorphous cellulose assumed to have no intramolecular hydrogen bonds. For the forms (b) and (c) shown in Figure 2, such a π–σ electron conjugate system as that in form (a), does not come about. Thus, to anticipate the shielding effect, only the electron density on the C_2 and C_6 carbons directly involved in the forms (b) and (c) need be considered. In the form (b), the cationized C_6 carbon must shift towards a higher magnetic field. The reverse applied for form (c).

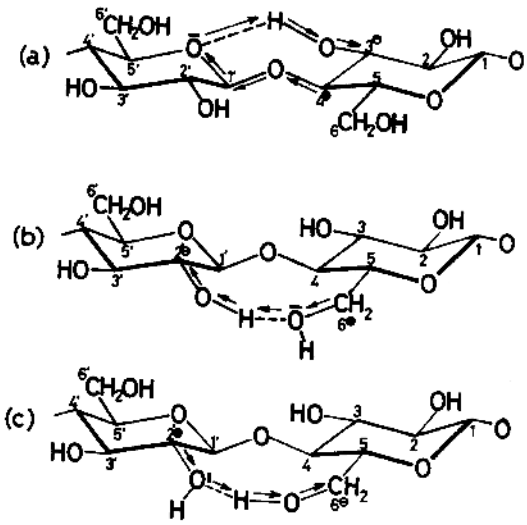

Figure 2. Schematic representation of intramolecular hydrogen bonds in cellobiose units: (a), O_3 H $\cdots$ O_5'; (b), O_2–H $\cdots$ O_6'; (c), O_6–H $\cdots$ O_2'; arrow mark denotes electron localization.

Figure 3a and c show a schematic representation of the NMR spectra for the C-2b sample as amorphous cellulose and the C-1 sample as cellulose with cellulose I crystals, respectively. Both were deducted from Figure 1. In the following we shall calculate the NMR

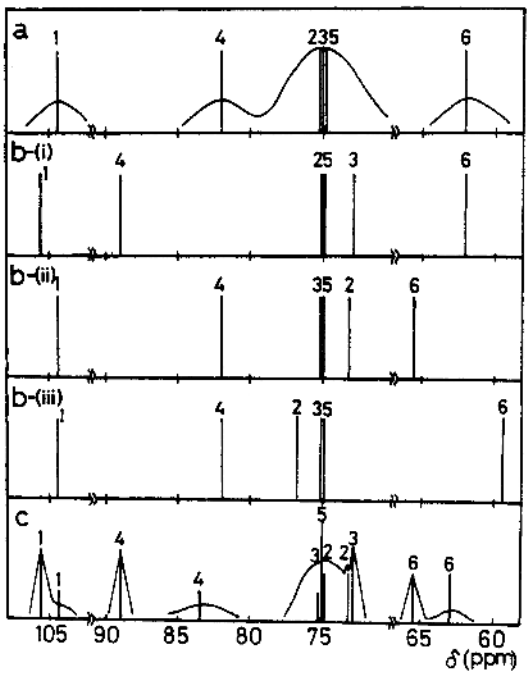

Figure 3. Schematic representations of experimental and hypothetical CP/MASS spectra of cellulose: (a), amorphous (C-2b, experimental); (b-(i)), cellulose I with the formation of a perfect O_3–H $\cdots$ O_5' intramolecular hydrogen bond (hypothetical); (b-(ii)), cellulose I with the formation of a perfect O_2–H $\cdots$ O_6' intramolecular hydrogen bond (hypothetical); (b-(iii)), cellulose I with the formation of a perfect O_6–H $\cdots$ O_2' intramolecular hydrogen bond (hypothetical); (c), cellulose I (C-1, experimental).

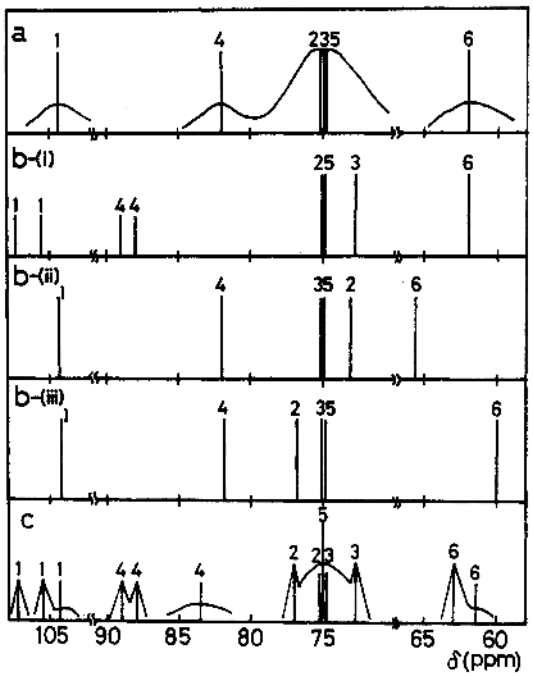

Figure 4. Schematic representations of experimental and hypothetical CP/MASS spectra of cellulose: (a), amorphous (C-2b, experimental); (b-(i)), cellulose II with the formation of a perfect O_3–H $\cdots$ O_5' intramolecular hydrogen bond (hypothetical); (b-(ii)), cellulose II with the formation of a perfect O_2–H $\cdots$ O_6' intramolecular hydrogen bond (hypothetical); (b-(iii)), cellulose II with the formation of a perfect O_6–H $\cdots$ O_2' intramolecular hydrogen bond (hypothetical); (c), cellulose II (C-2, experimental).

spectrum of each cellulose I sample. We assume that (1) all the cellulose molecules in a given sample solid, regardless of whether the molecules belong to the crystalline or amorphous region, can take only one of three possible types of intramolecular hydrogen bonds (see Figure 2), (2) in the crystalline region of cellulose I, only a specific value is allowed for the bond length of each type of intramolecular hydrogen bond (*i.e.*, O_3–H $\cdots$ O_5', O_2–H–O_6', and O_6–H $\cdots$ O_2') and (3) in the amorphous region, the distance of the intramolecular hydrogen bonds can be varied in a limited range from those in the crystal region. Figure 3-b-(i)—(iii) show the calculated line spectra of cellulose having the cellulose I crystalline form and three possible intramolecular hydrogen bonds. A comparison of Figure 3c with Figure 3b(i)—(iii) shows that cellulose of crystal form I consists of three types of cellobiose units with O_3–H $\cdots$ O_5' and O_2–H $\cdots$ O_6' intramolecular hydrogen bonds, and units without intramolecular hydrogen bonds.

Figure 4a—c show similar schematic NMR spectra for cellulose having cellulose II type crystals. Here, note that in cellulose II crystals, two different types of O_3–H $\cdots$ O_5' intramolecular hydrogen bonds exist, corresponding to two types of chain conformations of "bent" and "twist"[7] or two types of chain packings "parallel" and "anti-parallel". The other assumptions are the same as described for cellulose I. On the basis of a comparison

between Figure 4c and Figure 4a, b-(iii), we can conclude that the cellulose with cellulose II type crystals contains four types of cellobiose units: Units with O_3–H $\cdots$ O_5', O_2–H $\cdots$ O_6', and O_6–H $\cdots$ O_2' intramolecular hydrogen bonds, and units without intramolecular hydrogen bonds. It should be noted that O_6–H $\cdots$ O_2' intramolecular hydrogen bond, lacking in cellulose I, exists in cellulose II. This is probably related to the two "bent" and "twist" conformations or chain packings of "parallel" and "antiparallel" for cellulose II. The former may support the observations in this study, since in the latter case, rotational conformational change about C_5–C_6 is quite large and requires the considerable NMR peak shift of C_6 carbon not observed experimentally. The C_6 carbon peak can be considered to shift from the hypothetical line NMR peak positions by some specific intermolecular hydrogen bond.

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