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DISSOLUTION MECHANISM OF CELLULOSE IN N₂O₄-DMSO SYSTEM

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ABSTRACT

The dissolution mechanism of cellulose in the N₂O₄-DMSO system was studied by comparing ¹H-NMR spectra of cellulose/N₂O₄-DMSO solutions with those of methanol/N₂O₄-DMSO solutions. In the dissolved state, cellulose was found to form trinitrite ester, and this formation reaction was irreversible in DMSO.

1. INTRODUCTION

Recently many kinds of nonaqueous cellulose solvent systems have been found, and these findings have opened new fields of cellulose chemistry from both fundamental and practical points of view.

N₂O₄ systems as cellulose solvents were firstly found by Fowler et al¹⁾ in 1947, and then Nakao reported that DMSO, DMF and 28 other kinds of organic solvents dissolve cellulose when N₂O₄ is added²⁾. As to the applications of these cellulose solvent systems, Schweiger³⁾ and Philipp et al⁴⁾ reported that the N₂O₄-DMF system was a suitable medium for homogeneous sulfation of cellulose. Cellulose sulfate is known to have unique properties such as gelation, blood anticoagulant activity⁵⁾ and others. On the other hand, side-reactions including depolymerizations of cellulose were known to occur when N₂O₄-organic solvent systems were used as cellulose solvents for preparation of regenerated cellulose⁶⁻⁹⁾. Therefore, it is important to elucidate the dissolution mechanisms and the dissolved states of cellulose in these systems.

As to the dissolution mechanism, Schweiger³⁾ assumed the following equation (I) on the basis of reactions of low molecular alcohols with N₂O₄. Also Ishii showed by using ¹³C-NMR spectrum

of cellulose oligomers/N₂O₄-DMSO solution that cellulose was nitrited with N₂O₄ in the dissolved state¹⁰⁾. However, the degree of substitution (DS) of nitrite ester and the reversibility of the above reaction have not been proved. Generally it takes over 3 hrs to get good ¹³C-NMR spectra of polymer solutions, and this must cause some side-reactions of cellulose with HNO₃, when the cellulose/N₂O₄ solution systems were used for the measurement of ¹³C-NMR.

In this paper, therefore, the dissolution mechanism and the dissolved state of cellulose in the N₂O₄-DMSO system were studied by using ¹H-NMR.

2. EXPERIMENTAL

Samples and reagents: Avicel (commercially available cellulose powder, DP_v=250) was used as a cellulose sample. A N₂O₄/DMSO solution was prepared as follows. Liquid N₂O₄ was added into ca. 40 ml of dry DMSO in a 50 ml volumetric flask from a N₂O₄ cylinder. The amount of N₂O₄ added was determined by the weight increase, and the total volume was adjusted to 50 ml by the addition of new DMSO. The concentration of N₂O₄ was 0.194 g/ml. Avicel dissolved in this solvent within 30 min.

NMR measurements: JEOL JNM 4H-100 was used as a ¹H-NMR spectrometer. DMSO-d₆ and tetramethylsilane were used as a solvent and an internal standard, respectively, for NMR studies.

3. RESULTS AND DISCUSSION

3.1 Methanol/ N_2O_4 -DMSO system

Fig. 1 shows 1H -NMR spectra of methanol/ N_2O_4 -DMSO systems. The methyl proton and the hydroxyl proton of methanol appeared at 3.2 and 4.1 ppm, respectively, in the methanol/DMSO solution. When N_2O_4 equimolecular to methanol was added to this solution, a single peak due to the methyl proton of methyl nitrite appeared at 4.0 ppm. Simultaneously, the hydroxyl proton of methanol moved remarkably to the low magnetic field to appear at 17.3 ppm, and this strongly acidic proton was due to the proton of nitric acid in DMSO.

By the additions of more methanol to the above methanol/ N_2O_4 -DMSO solution having the molar ratio of 1:1 (MeOH: N_2O_4), the peak due to the methyl proton of free methanol appeared at 3.2 ppm together with that due to the methyl proton of methyl nitrite. Namely, these two kinds of methyl protons were distinguishable in the mixture by 1H -NMR. The peak due to the acidic proton moved to the high magnetic field with the increase in methanol added to the mixture. It is natural that the proton of HNO_3 and the hydroxyl proton of excess methanol appeared together as a single

peak when excess methanol was added, because these two kinds of protons are exchangeable each other.

These results indicate that the reaction of nitrite formation of methanol with N_2O_4 in DMSO is irreversible. Because, if this reaction were reversible or methyl nitrite and free methanol were exchanged quickly in DMSO, only one single peak due to these two kinds of methyl protons should be detected when excess methanol was added to the mixture, as shown in the case of another cellulose solvent systems, the SO_2 -amine-DMSO systems¹¹⁾. Therefore, the reactions of methanol with N_2O_4 in DMSO can be shown as the following equation (II). Namely, methanol reacts with N_2O_4 to produce quantitatively methyl nitrite and nitric acid in DMSO, and this reaction is irreversible in DMSO.

3.2 Dissolution mechanism of cellulose in N_2O_4 -DMSO system

Fig. 2 shows the 1H -NMR spectrum of the cellulose/ N_2O_4 -DMSO solution, in which the molar ratio of a hydroxyl group of cellulose to N_2O_4 was adjusted to 1:1. The acidic proton due to nitric acid appeared at 17.3 ppm, and this value is completely equal to that in the case of the methanol/ N_2O_4 -DMSO (MeOH: N_2O_4 = 1:1, by mol). Therefore, this NMR spectrum showed that the dissolved state of cellulose in N_2O_4 -DMSO is the same as that of methanol in N_2O_4 -DMSO, and cellulose was converted into cellulose nitrite. Furthermore, the chemical shift of the acidic proton in the cellulose/ N_2O_4 -DMSO solution indicates that the DS of nitrite groups in the cellulose

Fig. 1 1H -NMR spectra of methanol/ N_2O_4 -DMSO systems.

Fig. 2 1H -NMR spectrum of cellulose/ N_2O_4 -DMSO solution.

nitrite in the dissolved state is 3. Because, if some free hydroxyl groups of cellulose remain in the dissolved state, the acidic proton should appear at higher magnetic fields than 17.3 ppm by the proton exchange between nitric acid and free hydroxyl groups of cellulose as shown in the methanol/ N_2O_4 -DMSO systems.

Nakao²⁾ reported that more than 3 moles of N_2O_4 to a glucose residue of cellulose are required to prepare complete cellulose solutions, when N_2O_4 -organic solvent systems were used for the preparation of cellulose solutions. This supports the formation of cellulose trinitrite in the dissolved states, too.

^{13}C -NMR spectrum of the cellulose/ N_2O_4 -DMSO solution was also obtained, but was complicated a little as reported by Ishii¹⁰⁾. If cellulose trinitrite formed in the dissolved state, a simple spectrum like that of cellulose trinitrate should be obtained¹²⁾. Therefore, those complicated ^{13}C -NMR spectrum of the cellulose/ N_2O_4 -DMSO solution suggests that the DS of cellulose nitrite may be less than 3. However, it took 1 day's accumulation to get the ^{13}C -NMR spectrum, and this long accumulation time at 20°C must cause some side-reactions such as nitration of cellulose in the presence of such strong acid as nitric acid. These side reactions should bring about the complicated ^{13}C -NMR spectra of cellulose solutions in N_2O_4 systems. Therefore, ^1H -NMR methods are superior to ^{13}C -NMR for the investigation of the dissolved state of cellulose in the N_2O_4 -DMSO system, because the ^1H -NMR spectrum of the cellulose

solution can be obtained in a few minutes just after cellulose is dissolved, and some effects due to side-reactions can be excluded as much as possible.

Consequently, the dissolution mechanism and the dissolved state of cellulose in the N_2O_4 -DMSO system can be shown as the following equation (III).

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四酸化二窒素・ジメチルスルホキシド系 に対するセルロースの溶解機構

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非水系セルロース溶剤の一つである標記の系に対するセルロースの溶解機構を, ^1H -NMRを用いて検討した。同じ系に溶かしたメタノールの ^1H -NMR スペクトルと

比較することにより, セルロースは三置換亜硝酸エステルとなって溶解していることを明らかにした。