JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 2467–2471 (1967)

Reaction of α-Cellulose with $SbCl_3$–KOH–$AsCl_3$

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Synopsis

α-Cellulose dissolves in a mixture of $SbCl_3$, KOH, and $AsCl_3$. The resulting product as identified by PMR and infrared spectroscopy is α-D-glucose. This product is unexpected, and an explanation for its formation is suggested.

INTRODUCTION

$SbCl_3$ and $AsCl_3$ are amphoteric solvents giving self-dissociation as shown in eq. (1).

$$2SbCl_3 \rightleftharpoons SbCl_2^+ + SbCl_4^- \quad (1)$$

Inorganic compounds such as $FeCl_3$ easily dissolve in both halides, and the iron salt can be considered as an acid in these solvent systems.

Szymanski et al.[1–4] have reported the use of these halides as solvents for polymers and other organic compounds. They showed that the halides had a high capability for dissociating hydrogen bonded compounds. For example, water in $AsCl_3$ gives an infrared spectrum which closely resembles that of water vapor.

Neither solvent nor a mixture of them will dissolve α-cellulose. However, it was found that addition of 5% by weight of KOH to a 50:50 mixture of the two halides did dissolve the cellulose. We shall report the results of this study here.

EXPERIMENTAL

Reaction of α-Cellulose with Solvent $SbCl_3$–$AsCl_3$–KOH

The α-cellulose used in this reaction was of the highest purity obtainable. The $SbCl_3$ and $AsCl_3$ were both Baker and Adamson reagent grade products. The KOH used was a Fischer certified reagent. The fresh reagents were stored in a desiccator over anhydrous $CaCl_2$.

The solvent system for the reaction was prepared by mixing a 50:50 mixture (by weight) of $SbCl_3$ and $AsCl_3$. After complete mixing had occurred, KOH equal to 5% by weight of the $SbCl_3$ was added. The entire mixture was then heated gently until a clear solution was obtained. The solvent system remained a liquid at room temperature. It is of

interest that 5% KOH in $SbCl_3$ also is a liquid at room temperature although both constituents are solids.

The reaction of the α-cellulose in the solvent system was carried out by cutting the α-cellulose into small pieces and placing them into the solvent. The solvent plus cellulose was placed in a glass vial and heated in a water bath at 45°C. As the pieces of α-cellulose appeared to go into solution, more α-cellulose was added to the glass vial. This procedure was continued until saturation occurred.

We could not exclude moisture completely, so that the mixture contained an equilibrium amount of water. Presumably this was the source of water necessary for the hydrolysis of cellulose.

Measurement of the PMR Spectra

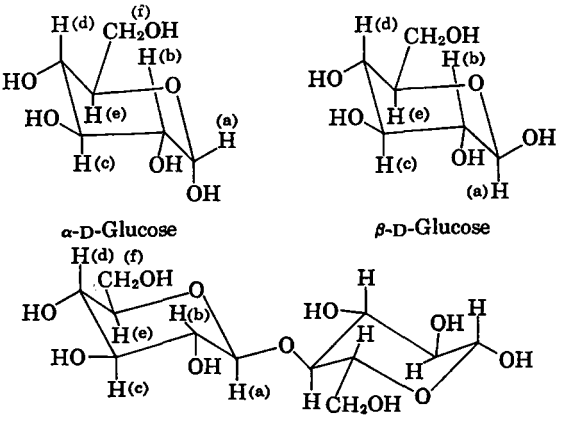
The PMR spectra were run on a Varian A-60 analytical spectrometer operating at 60 Mc./sec. A sweep width of 500 cps was sufficient to record all chemical shifts present. The spectrum was run at approximately 35°C. (the temperature of the magnet gap). All chemical shifts are referenced to an internal tetramethylsilane (TMS) standard.

RESULTS AND DISCUSSION

The PRM spectrum of α-cellulose in the solvent $SbCl_3$–KOH–$AsCl_3$ is shown in Figure 1. The infrared spectrum of this same mixture is shown in Figure 2.

The infrared spectrum shown in Figure 2 was compared to that of α-cellulose as measured for a KBr pellet and by A.T.R. (attenuated total reflectance). There were distinct differences, and further searching of the infrared literature indicated that the spectrum shown in Figure 2 matches that of α-D-glucose.

This is confirmed by the PMR spectrum shown in Figure 1. The assignments of the signals observed is as follows, based on the structural formulas for α-D-glucose, β-D-glucose, and cellobiose.



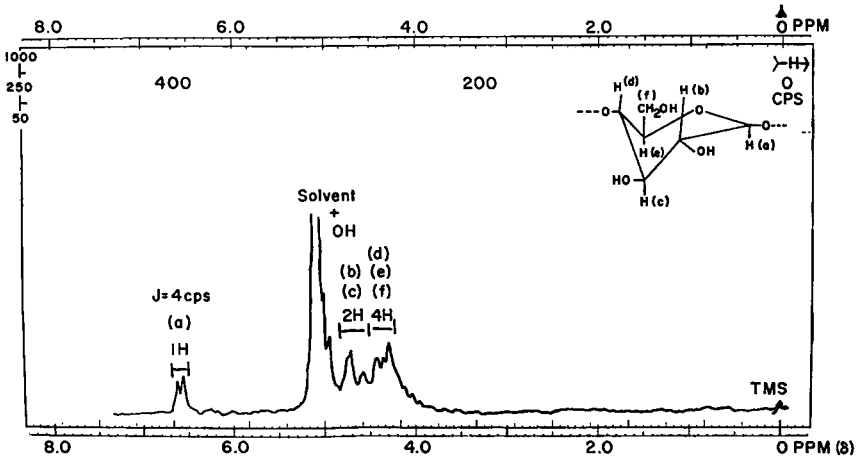


Fig. 1. PMR Spectrum of α-cellulose dissolved in KOH–$SbCl_3$–$AsCl_3$. Filter bandwidth, 1.0 cps; rf field, 0.07 mG.; sweep time, 250 sec.; sweep width, 500 cps; sweep offset, 0 cps; spectrum amp., 63.

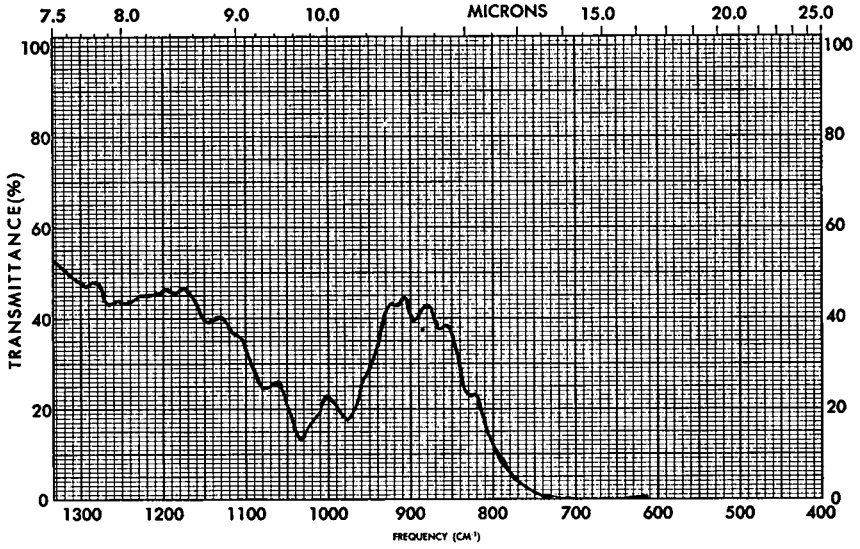


Fig. 2. Infrared spectrum of α-cellulose dissolved in KOH–$SbCl_3$–$AsCl_3$.

The low field doublet is assigned to the anomeric proton a. This proton is expected to resonate at a lower field than any other since it is the only proton next to two oxygens.

The resonance for protons b and c is the second lowest field signal. Although the environments of protons b and c are not exactly the same, they are similar enough that one would expect them to resonate at approximately the same position. The environments are similar because they both are hydrogens of a secondary alcohol; also there is a C=O bond on either side of the carbon to which they are joined.

The protons d, e, and f are assigned to the area from approximately 4.0 to 4.45 ppm. These four protons are expected to absorb at a higher frequency than the b and c protons for the following reasons. The f protons both belong to a primary alcohol, not a secondary alcohol like b and c. The d and e protons are in an environment that is not as deshielding as b and c, since there is no oxygen atom attached to the carbon atoms on either side.

The anomeric proton a appears as a low field doublet with a coupling constant of 4 cps. A coupling constant of 4 cps implies that the a and b protons are axial–equatorial, or equatorial–equatorial to one another. A J value of 8 cps would indicate an axial–axial configuration.

For α-cellulose, the a and b protons are locked in an axial–axial configuration. If the α-cellulose had been unassociated in the solvent, then the low field doublet would be expected to be 8 cps.

The observed spectrum has a doublet of approximately 4 cps separation. This can only mean an axial–equatorial orientation for the a and b protons, since for the unassociated of cellulose only the hydrogen on the endgroups can rotate. It was thus concluded that a breaking of bonds between glucose units must occur to obtain the observed product. One would expect the bulky OH groups, if the cellulose were split into glucose units, to go into the equatorial position, since in this situation there is less nonbonded interaction. This would place the a proton in the axial position where a coupling of 8 cps would be observed.

If the α-cellulose were broken into groups of two or more glucose units (cellobiose, cellotriose, etc.) there would be two possible positions for the anomeric a proton (if one disregards stereochemical preferences). The ones at the ends would be axial or equatorial, and the ones in between the glucose units would necessarily be axial. This would give rise to two different environments for the a proton. If the PMR shifts were large for the protons in these two configurations two distinct doublets would be expected, one for the axial–axial case and one for the axial–equatorial case. If the shift differences were small, the doublets would be expected to overlap, giving either a broad band, or a doublet with fine structure. For many related compounds the axial protons resonate at approximately 0.5 ppm to higher field than an equatorial proton, the case of two doublets is the more probable situation. Since we observe a doublet of 4 cps we must conclude all the a protons are in an equatorial position and that the cellulose has been broken down in our solvent system to single α-D-glucose units. The infrared spectrum confirms this assignment.

α-D-Glucose is known to mutarotate in aqueous solution to a mixture of the α and β forms, with the β-D-glucose form predominating. When a PMR spectrum of the mixture of α and β forms was determined with H_2O as the solvent, the anomeric hydrogen showed up as a broad peak rather than a doublet. This is as expected. Since there is an equilibrium between the α and β forms, one would expect a rapid exchange between the two forms with a consequent broadening of all peaks and a breakdown

of the individual 4 cps and 8 cps doublet into a broad peak. As expected, since there is an equilibrium, there is a breakdown of fine structure and the resonances occur over a slightly larger chemical shift range than if the NMR spectrum was of only one compound.

When the same mixture is run in the $SbCl_3$–KOH–$AsCl_3$ solvent, it is found that the broad peak becomes a doublet of 4 cps and fine structure appears, indicating that the mixture has been converted to the unfavored α-D-glucose. It is the same spectrum as that obtained when α-cellulose was placed in the solvent system, and as explained previously, was shown to be that of α-D-glucose.

A possible explanation as to the formation of α-D-glucose in our solvent system would be that a complex forms between the glucose and halides. This complex holds the a protons in the equatorial position giving the glucose unit the configuration that exists for the α-D form. This type of charge transfer complex would not be unexpected for solutions in $SbCl_3$.

We are attempting to obtain further data on the existence of this complex.

At the suggestion of the reviewer we examined in our solvent system one sugar derivative having an axial–equatorial configuration such as α-D-glucose. This was α-D-glucose pentaacetate. We found no change in the coupling constant observed for the C_1 proton in our solvent compared to the spectrum measured in deuterated chloroform. It is concluded therefore that our solvent system does not change the coupling constant of α-D-glucose from that observed in conventional solvent systems.

References

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Résumé

α-Cellulose se dissout dans un mélange $SbCl_3$–KOH–$AsCl_3$. Le produit résultant, identifié par PMR et par spectroscopie infrarouge, est l'α-D-glucose. Ce produit est inattendu et l'explication de sa formation est suggérée.

Zusammenfassung

α-Cellulose löst sich in einem $SbCl_3$–KOH–$AsCl_3$-Gemisch, das erhaltene Produkt wird durch PMR- und Infrarotspektroskopie als α-D-Glukose identifiziert. Eine Erklärung für die Bildung dieses unerwarteten Produktes wird gegeben.

Received December 29, 1966
Revised April 23, 1967
Prod. No. 1637