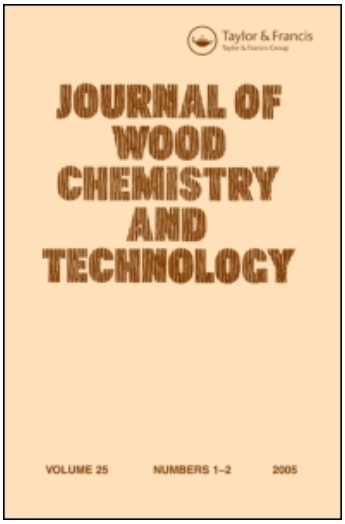

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Direct Evidence for Covalent Bonding Between Ketene Dimer Sizing Agents and Cellulose

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DIRECT EVIDENCE FOR COVALENT BONDING BETWEEN KETENE DIMER SIZING AGENTS AND CELLULOSE[1]

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ABSTRACT

The heterogeneous reactions of fatty acid ketene dimer with methyl α-D-glucopyranoside, maltose, cellobiose, microcrystalline cellulose and a bleached kraft pulp have been investigated under base catalyzed conditions in N,N-dimethylformamide (DMF). The reaction products have been examined by ^{13}C-NMR and/or infrared spectroscopy. The spectral data provide the first direct evidence for β-ketoester formation with these substrates.

INTRODUCTION

Alkyl ketene dimer (AKD) sizing agents were introduced to the paper industry in the 1950's. Since that time, the sizing mechanism has been a subject of controversy. Published results can be most consistently explained in terms of the originally suggested mechanism[2] of covalent bond formation through the cellulose hydroxyl groups.

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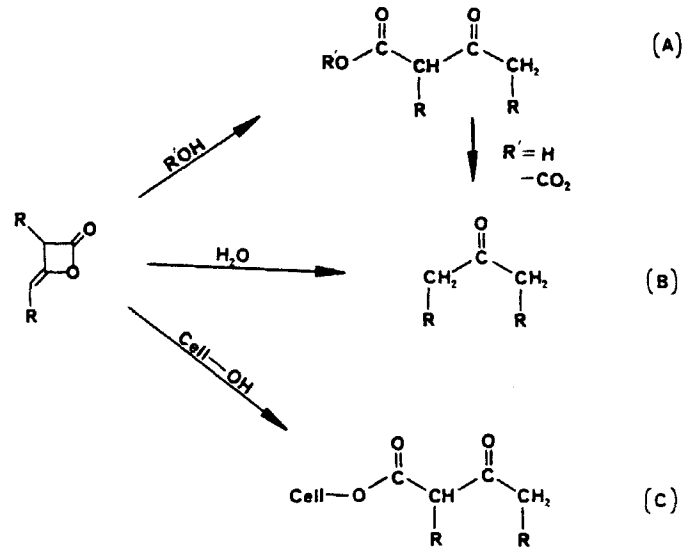
Work with ketene dimer treated paper has not demonstrated bond formation[3-6] primarily because of instrumental limitations. To realistically model papermaking conditions, the amount of AKD applied should be low, typically near 0.1% based on the dry pulp. For internally sized paper, difficulties with size retention can reduce this level significantly[7]. At these levels, the available spectroscopic techniques lack the necessary sensitivity to directly observe the anticipated bond within the fiber matrix.

The evidence generally cited to support the reaction model (Scheme 1, path C) has been based on extraction studies[5,8,9] some employing radioactive AKD. From these experiments, the reaction of AKD with cellulose in formed sheets was inferred by changes in the proportions of extractable vs unextractable AKD (radioactivity) as a function of various parameters, including time, drying conditions, and pH. Unfortunately, extraction experiments do not provide direct demonstration of chemical bonding with cellulose hydroxyls. Other mechanisms could be invoked to rationalize the results, for example hydrogen bonding[4] or other types of complex formation[10] or polymerization of the AKD on the fibers[6].

Model studies [11,12] have not been successful in finding evidence for covalent bond formation either. Ketene dimers useful for sizing paper are very hydrophobic, and the formation



SCHEME 1 R = $C_{14}H_{29}$ and/or $C_{16}H_{33}$

(A) R' = Methyl, Ethyl, Isopropyl

(C) Cell = Cellulose or Cellulose Model

Paths (A) and (B) have been well documented, but path (C) has never been observed.

of homogeneous solutions containing both AKD and the hydrophilic cellulose models is difficult. This phase separation can lead to experimental difficulties. While interphase reactions are well-known, finding the proper conditions can be very difficult. In one study[11] evidence of reaction between octadecyl ketene dimer and methyl α-D-glucopyranoside was sought under neutral heterogeneous conditions. These workers[11] also tried cellulose pulp in a pyridine slurry without success. In another case[12]

acidic homogeneous conditions were found, but again no reaction was observed between tetradecyl ketene dimer and the model compound methyl ß-cellobioside.

In this work, the reactions between cellulose model compounds and alkyl ketene dimer were investigated in order to find conditions under which the desired reaction would occur. After successful realization of this goal, these conditions were applied to two cellulose substrates. While the reaction conditions ultimately found in these studies are admittedly not papermaking conditions, it was demonstrated that reaction does occur. Work is currently in progress in these laboratories which more closely simulates papermaking conditions.

RESULTS AND DISCUSSION

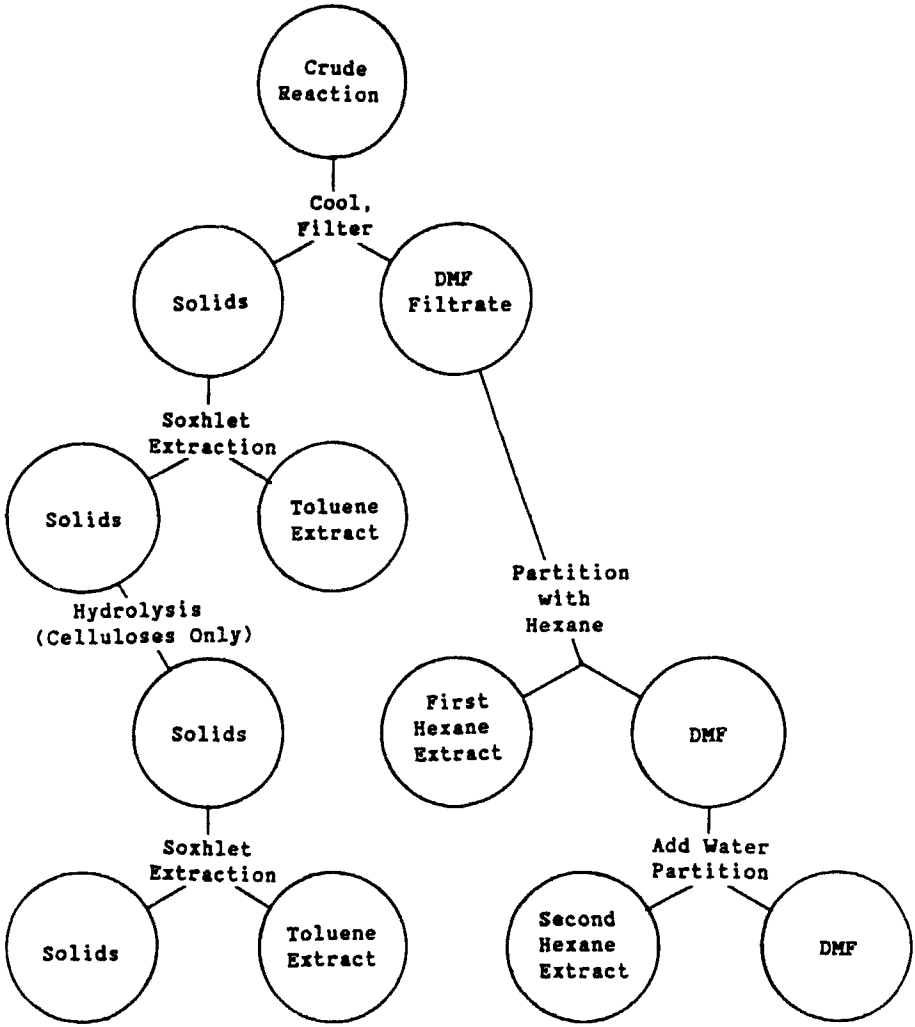
Cellulose Model Compounds

The choice of solvent and use of a basic catalyst proved to be as important to the results as the product isolation procedures. N,N-Dimethylformamide was chosen for the reaction medium because it is known to swell cellulose, thus modeling the effects of water on cellulose during papermaking. The basic catalyst (N-methylmorpholine) was chosen to mimic the soluble alkalinity arising from the use of calcium carbonate fillers generally found in ketene dimer sized papers. Pyridine was avoided because it reacts with AKD, forming a fairly stable adduct.[13]

Throughout the following discussion, products will be referred to according to their origin as described in Scheme 2. Material balances for the model reactions are given in Table 3 (see Experimental Section).

When the mixture from the reaction of methyl α-D-glucopyranoside and alkyl ketene dimer was cooled, a solid precipitated which was isolated and identified as unreacted methyl α-D-glucopyranoside[14] representing recovery of 25% of the original charge. The first hexane extracts (Scheme 2) yielded a much larger quantity of a waxy, low melting solid (Table 3). The infrared and ^{13}C-NMR spectra of this material are reproduced in Figures 1 and 2, respectively.

The primary features of interest in the infrared spectrum are the carbonyl stretching bands located at 1748 and 1716 cm^{-1}. These correspond to the ester and ketone carbonyls, respectively, of a nonenolized β-ketoester[15,16] Additional evidence for the absence of enolization is discussed in connection with the ^{13}C-NMR data below. The other distinct features in the IR spectrum include the weak OH stretch at 3430 cm^{-1}, and a pair of very strong absorbtions at 2851 and 2925 cm^{-1} due to the symmetrical and asymmetrical CH_2 stretching modes, respectively, characteristic of linear hydrocarbons[16] While absorbtions in this frequency range are also found in the unmodified methyl α-D-glucopyranoside, they are much weaker.



SCHEME 2 Flow Chart for Reaction Work-up

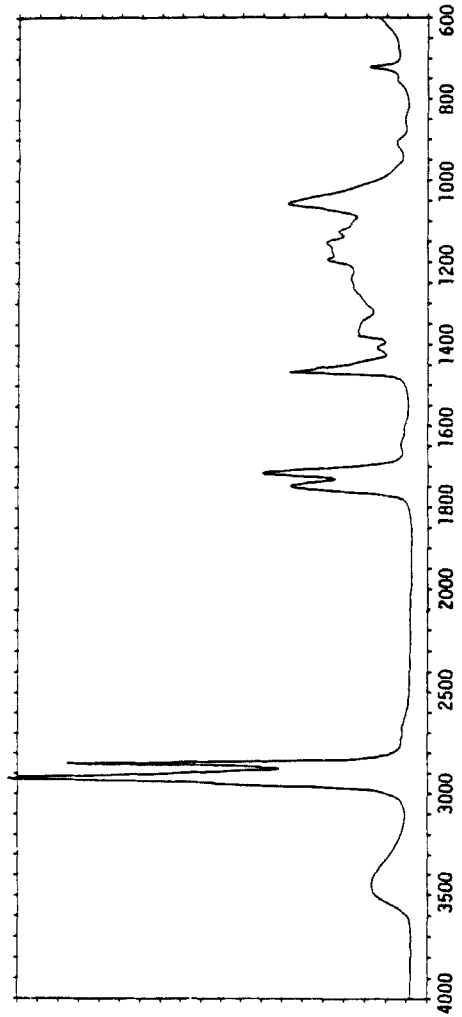


FIGURE 1 Infrared Spectrum of AKD-Reacted Methyl α-D-Glucopyranoside

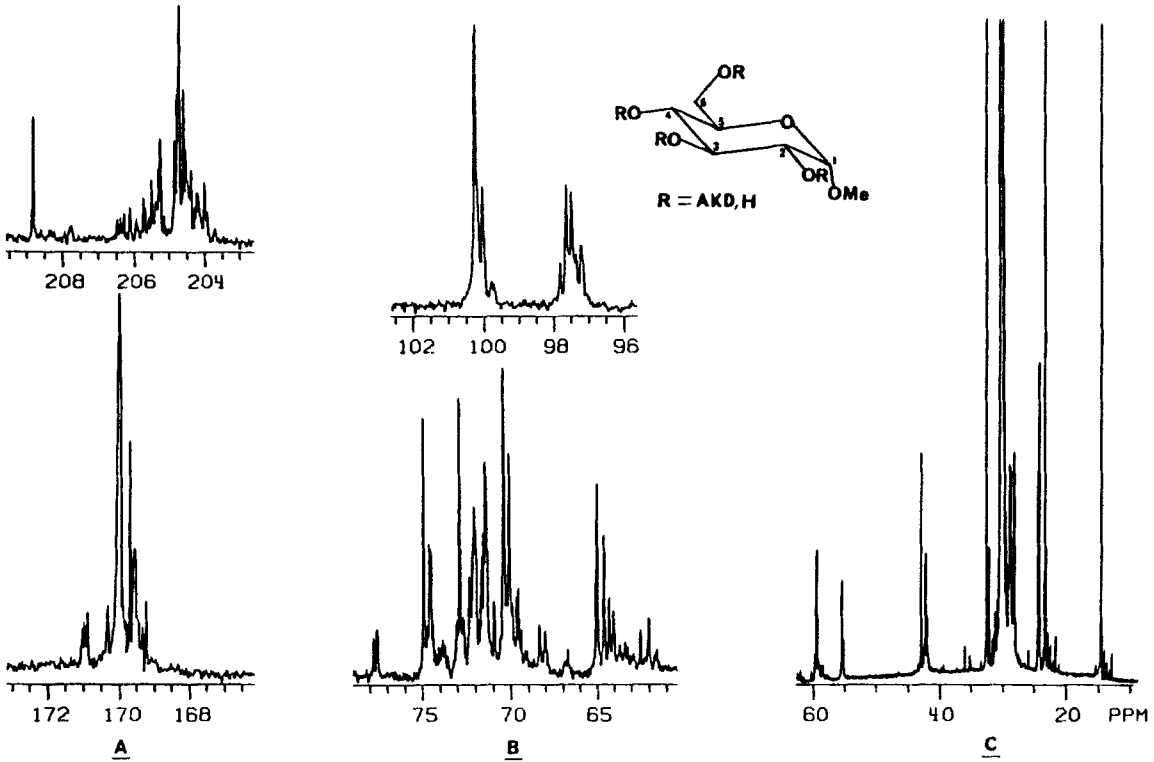


FIGURE 2 90 MHZ ^{13}C-NMR Spectrum of AKD-Reacted Methyl α-D-Glucopyranoside. (A) Carbonyl Region, (B) Saccharide Region, (C) Aliphatic Region

TABLE 1
Carbonyl Infrared Absorbances for Reaction Products of Alkyl Ketene Dimer with Various Substrates

Substrate[a]	Infrared Absorbance Ester	Ketone	Ester CO:OH Absorbance Ratio[17]
Methyl α-D-Glucopyranoside	1748cm^{-1}	1716	2.5
Cellobiose: First Extract	1750	1713	2.5
Second Extract	1743	1711	0.9
Maltose: First Extract	1748	1714	2.7
Second Extract	1743	1708	0.9
Microcrystalline Cellulose	1748	1713	<1[b]
Bleached Kraft Pulp	1752	1719	>2[b]

[a] AKD ester CO: 1848 cm^{-1}, stearone ketone CO: 1706 cm^{-1}
[b] Measured from DRIFTS difference spectra, see next section

Additional absorbtions attributed to different CH_2 vibrational modes are located at 1467 and 722 cm^{-1}. A full discussion of the various CH_2 vibrational modes can be found in Reference 16. The relative intensities of the ester carbonyl (CO)[17] and the unsubstituted OH absorbtions is near 2.5 (Table 1), and can be related to the degree of substitution, vide infra.

The complete ^{13}C-NMR spectrum of this material is illustrated in Figure 2. It exhibits a complex set of signals in the "saccharide region"[18] along with resonances due to ester and ketone functionalities[19]. Had there been no reaction, the ring carbon spectrum would have consisted of a simple six line pattern in the 60-100 ppm region, and no signals due to carbonyl or aliphatic carbons would have been present. Indeed,

if there had been no reaction, the product would not have been soluble in benzene-d_6 (NMR solvent).

The most distinctive resonances for diagnosing saccharide substitution patterns are those of C_1 (when the C_2 hydroxyl is unsubstituted, it is near 99 ppm) and C_6 (when the C_6 hydroxyl is unsubstituted, it is near 62 ppm).[18] See Figure 2 for numbering of the glucopyranose ring.

While this ^{13}C-NMR spectrum is too complex for a complete analysis, it can still provide structural information. Splitting of the C_1 resonance into two major peaks is significant. The signals centered near 100.2 ppm are due to C_1 in species with no substitutent on the C_2 hydroxyl, while the signals centered near 97.5 ppm are due to C_1 in species with a substituent on the C_2 hydroxyl. In both cases, the fine structure present is due to a second (or third) substituent elsewhere on the ring.

Similarly, the multiplicity of signals between 60 and 65 ppm, all due to C_6, is also consistent with a mixture of multiple substitution products.[18] Finally, the two sets of resonances near 170 ppm and 205 ppm are carbonyl signals, consistent with a family of related ß-ketoesters. The splittings of these carbonyl resonances are less diagnostic than those of the ring carbons due to a smaller data base for comparison. The isolated resonance near 209 ppm is due to a low level of stearone contamination (see B in Scheme 1).

The absence of the enol form in this product is supported by the calculation of expected chemical shifts, based on empirical additivity rules.[19] These calculations suggest that the resonances for both enol carbon-carbon double bond carbons should appear near 135 ppm. No resonances are visible above the noise level between 100 and 170 ppm (except for the solvent benzene-d_6), ruling out this type of structure as a major species.

Cellobiose was not soluble in DMF under these reaction conditions, and not surprisingly, a larger amount of solid material was present after the AKD had been consumed (Table 3, Experimental Section). Extraction of the solid with toluene separated it into unreacted cellobiose (76% recovered) and stearone (equivalent to 22% recovered, see B in Scheme 1). The first hexane extract yielded a large amount of a waxy, low melting solid (Table 3), and the second hexane extract yielded a much smaller amount of a higher melting, glassy solid (Scheme 2). While the infrared spectra of both isolates were similar, they differed in some important details (Figure 3), specifically in their relative OH and ester CO intensities.

In Figure 3, the scaling factors of the infrared spectra have been adjusted to make the ester carbonyl absorbtions approximately equal.[17,21] The only significant differences[17] between the spectra observed this way are their

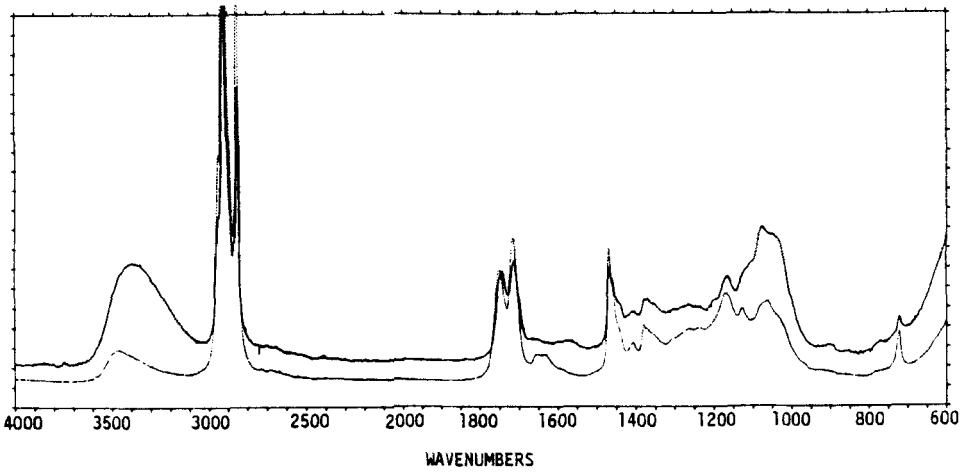


FIGURE 3 Infrared Spectra of AKD-Reacted Cellobiose: Lower Trace First Hexane Extract, Upper Trace Second Hexane Extract

ester CO:OH absorbance ratios (~ 1750:3400 cm^{-1}). For the first hexane extract (lower trace) this ratio is near 2.5, and near 1.0 for the second hexane extract (upper trace).

Qualitatively the product from the first hexane extract appears to have fewer free hydroxyl groups than the product from the second hexane extract.[21] Stated differently, the average degree of substitution (DS) of the first product is higher than that of the second. Elemental analysis of the first product is consistent with an average DS of 2 (see Table 2).

TABLE 2
Results of Elemental Analyses for First Hexane Extract Products

Saccharide	Calculated Composition for DS of 2:	%C	%H	Found: %C	%H
Methyl α-D-glucopyranoside	$C_{75}H_{142}O_{10}$	74.88	11.81	74.35	11.58
Cellobiose	$C_{148}H_{278}O_{19}$	75.34	11.78	76.01	11.69
Maltose	$C_{148}H_{278}O_{19}$	75.34	11.78	75.38	11.88

For there to be more material of higher DS (approximately 13:1 in this case), the second and subsequent acylations have to be faster than the first under these base-catalyzed, heterogeneous conditions. Enhanced reactivity after the initial acylation can be readily accounted for if it is assumed that the reactions take place exclusively at the interphase boundary. The lack of product formation reported recently[12] between tetradecyl ketene dimer and methyl ß-cellobioside cannot be attributed to steric hindrance.

A similar situation was found in the reaction of DMF soluble maltose monohydrate with AKD. After separation of the expectedly large amount of stearone, two product fractions were isolated based on solubility differences (Table 3). The product from the first hexane extract had a higher DS according to the infrared spectra, as determined above, than that from the second hexane extract. Again, there was more product isolated from the first hexane extract than the second. Analysis of the two spectra in Figure 4 is similar to that of Figure 3[17] above.

Table 3. Material Balance and Product Distribution for Model Reactions[A]

Reactants Charged	Second Solids	First Toluene Extract	First Hexane Extract	Second Hexane Extract	Total Recovery
Methyl α-D-Glucopyranoside 9.70 g (20.0 mmol) Alkyl Ketene Dimer 25.00 g (44.7 mmol)[B]	Methyl α-D-Glucopyranoside 3.76 g (5.2 mmol)	Negligible	29.94 g	Negligible	33.69 g (97.2%)
Cellobiose 17.20 g (50.0 mmol) Alkyl Ketene Dimer 25.80 g (46.1 mmol)[B]	Cellobiose 13.03 g (38.2 mmol)	Stearone 4.89 g (10.25 mmol)	21.29 g	1.64 g	41.10 g (96.2%)
Maltose Monohydrate 10.00 g (27.8 mmol) Alkyl Ketene Dimer 7.50 g (11.1 mmol)[B]		Stearone 3.39 g (7.1 mmol)	3.65 g	1.07 g	8.11 g (46.4%)[C]

[A] See Scheme 2 for column heading definitions.

[B] Molar charge based on 90% assay of AKD.

[C] No effort was made to recover unreacted maltose dissolved in the DMF.

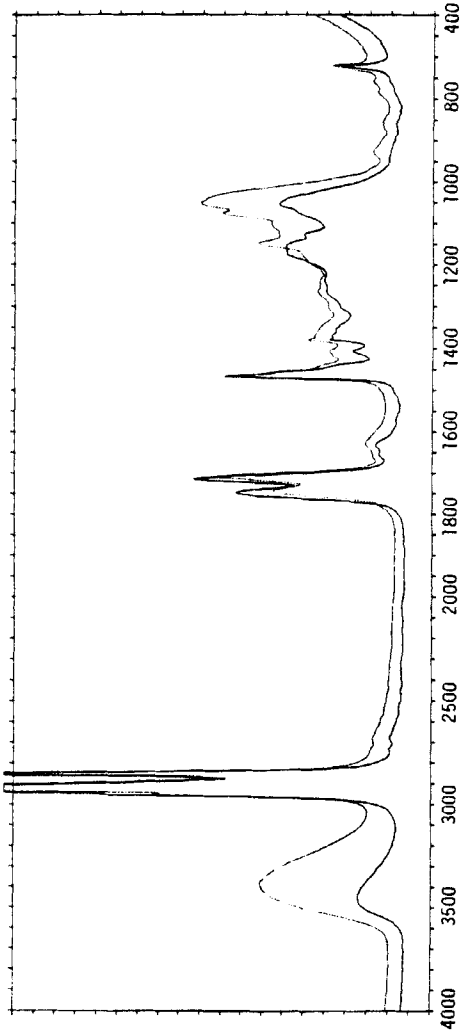


FIGURE 4 Infrared Spectra of AKD-Reacted Maltose: Lower Trace First Hexane Extract, Upper Trace Second Hexane Extract

The lower traces in Figures 3 and 4, and the infrared spectrum from methyl α-D-glucopyranoside in Figure 1, show similarly high ester CO:OH ratios (see Table 1), consistent with their elemental analyses. Although the signals are broader, and therefore less well resolved, comparisons between the ^{13}C-NMR spectra of the two product fractions isolated from each disaccharide show features similar to those found in the methyl α-D-glucopyranoside spectrum (Figure 2), especially the presence of ester and ketone carbonyl resonances.

Cellulose Substrates

After successfully demonstrating ester formation with the model compounds, two cellulose substrates were chosen for reaction under the same general conditions, viz. microcrystalline cellulose (MCC), and a 3:1 mixed hardwood/softwood bleached kraft pulp (BKP), typical of pulp furnishes used in paper manufacture. For these two substrates, only the insoluble portions of the product mixtures have been examined thoroughly.

After isolation, the MCC solids were extracted for at least 16 hrs with toluene (Soxhlet) to remove unreacted AKD, stearone, and DMF which may have been present. A portion of this extracted material was examined by DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) for new surface functionality. With this technique, sensitivity on the order of 0.5 wt% can be obtained by difference spectra (untreated substrate subtracted from treated substrate). New features present in the treated MCC

spectrum were so strong that a spectral subtraction was not necessary for their visualization.

In Figure 5, a narrow region of the unsubtracted DRIFT spectrum of the AKD treated MCC has been reproduced as the bold (middle) trace. The very strong feature at 1428 cm^{-1} is from the cellulose substrate (CH_2 stretch from C_6[22]), and is therefore useful as a constant internal standard for comparing signal intensities among different samples.[21] The features of interest in this spectrum are located at 1748 and 1713 cm^{-1}, and like in the model substrates, are due to the ester and ketone carbonyl groups of a nonenolized β-ketoester.[14,15] The small absorbance near 1650 cm^{-1} in this spectrum is due to residual DMF.[16]

A portion of the AKD-modified MCC was subjected to mild hydrolysis under (sequentially) basic and acidic conditions. After a methanol wash and exhaustive extraction with toluene, the solids had lost ca. 7 wt%. Material corresponding to this weight loss was isolated from the toluene extract, and identified as stearone by comparison to an authentic sample. The DRIFT spectrum of the MCC solids after hydrolysis and extraction is shown as the light (lower) trace in Figure 5. Scaling the 1428 cm^{-1} internal marker intensity close to that of the bold (middle) trace clearly shows a decrease in the β-ketoester carbonyl intensities after partial hydrolysis. The small sharp

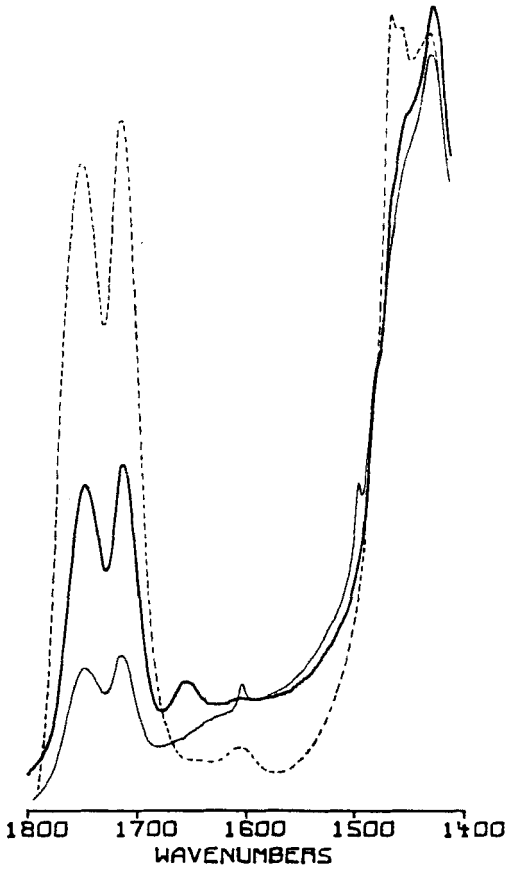


FIGURE 5. DRIFT Spectra of AKD-Reacted Celluloses, see text for discussion

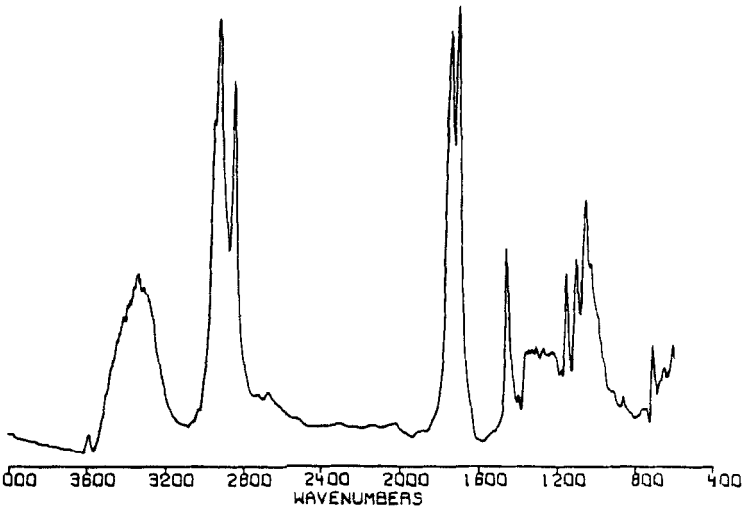


FIGURE 6. DRIFT Difference Spectrum of AKD-reacted Bleached Kraft Pulp

features in this spectrum at 1600 and 1500 cm^{-1} are due to residual toluene left in the sample.[16]

Treatment of the BKP-AKD reaction product was similar to that of the MCC substrate. However, the level of functionalization obtained for the BKP[23] substrate was much higher than in the case of the microcrystalline cellulose (dashed trace in Figure 5). Figure 6 is the DRIFT difference spectrum of the AKD-treated bleached kraft pulp. Overall, this spectrum bears a strong resemblance to the model compound transmission spectra (Figures 1, 3, and 4). It is interesting to note that the relative ester CO:OH ratio in this spectrum is greater than 2.

Comparison with the models in this regard suggests the possibility of (surface anhydroglucose unit) degrees of substitution greater than 1 (Table 1).

CONCLUSIONS

This work has presented the first direct spectroscopic evidence (both infrared and ^{13}C-NMR) that the higher alkyl ketene dimers react with cellulose model compounds, as well as with cellulose itself. It has also been shown that for the model compounds steric hindrance does not seem important.[12] In the presence of a large molar excess of saccharide reactive sites, conditions where a single reaction is predicted per (anhydro)glucose unit by statistics, multiple reaction with AKD is favored in these heterogeneous reaction conditions.

EXPERIMENTAL

Materials

Methyl α-D-glucopyranoside, D-maltose monohydrate, cellobiose, and N-methylmorpholine were obtained from Aldrich Chemical Co. and used as received. Avicel PH105 microcrystalline cellulose (MCC) was obtained from FMC Corp. and azeotropically dried with toluene immediately before use. The cellulose pulp furnish was a 3:1 blend of hardwood and softwood bleached kraft dry lap pulps (BKP), beaten at 2.5% consistency to a Schopper-Riegler freeness of 450 ml. It was washed sequentially

with methanol and toluene, exhaustively extracted with toluene, and used while toluene-wet. Alkyl ketene dimer, taken from a sample of commercial flake made from a 1:1 palmitic/stearic acid mixture, and recrystallized from acetone, had a 90% assay, the remainder being anhydride. N,N-Dimethylformamide, toluene, hexane, methanol, NaOH pellets, anhydrous magnesium sulfate, and concentrated HCl were all J. T. Baker reagent grade, and except for the DMF, used as received. The DMF was batch dried over 1/16" Linde 3Å molecular sieves (activated at 200°C under a 50 ml/min flow of dry N_2) at a 5:1 weight ratio, and then passed through a column (60 x 2.5 cm) of fresh sieves prior to use.

Transmission infrared spectra were recorded on a Perkin-Elmer 983 infrared spectrophotometer on sodium chloride plates in the absorbtion mode at 3 cm^{-1} resolution. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded with a Nicolet 6000, using a Harrick diffuse reflectance attachment; 2000 scans were transformed at 2 cm^{-1} resolution for each spectrum. ^{13}C-NMR spectra were obtained on a Nicolet NT 360 WB spectrometer at 90.55 MHz at ambient temperature, on samples of 20-30 wt% concentration in benzene-d_6 with a pulse angle of 70°, pulse delay of 3 sec, and sweep width of $\pm$ 10,000 Hz.

Elemental analyses were performed by Micro Analysis Inc., Wilmington, DE.

General Procedures

Reaction with AKD: The substrate was suspended or dissolved in 2-10 ml/g dried DMF containing 5 wt% of N-methylmorpholine, based on substrate, and heated to 90-95°C. Insoluble substrates were held at temperature for 1 hr before addition of neat AKD. After being held at temperature overnight, the reaction mixture was cooled to below 20°C. Any solids present were collected and washed sequentially with cold DMF and methanol. The clear DMF (filtrate) was extracted with several portions of hexane, which were combined, washed with distilled water and sodium chloride solution, dried over anhydrous $MgSO_4$, and concentrated at reduced pressure. The extracted DMF was diluted with up to 5 volumes of water and extracted again with hexane as above. The MCC solids collected from the crude reaction mixture were extracted (Soxhlet) with toluene overnight. The BKP solids were extracted sequentially with toluene and 95% ethanol for at least 16 hrs each. The remaining solids and the toluene extracts were examined by infrared spectroscopy for identification; see Scheme 2.

Hydrolytic Studies: A portion of the material to be hydrolyzed was suspended in 2:1 aqueous DMF and the pH adjusted to 9 with NaOH. For MCC, the mixture was heated to reflux for 4 hrs, allowed to cool, acidified to pH 2 with conc. HCl and again heated to reflux 1 hr. For BKP, these times were increased to 16 and 4 hours. After cooling, the MCC solids were filtered,

washed with water and cold methanol and extracted (Soxhlet) with toluene overnight. The BKP solids were extracted sequentially with toluene and 95% ethanol for at least 16 hrs each. The remaining solids and toluene extract were examined by infrared spectroscopy.

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