

Liquid-Chromatographic Determination of Rate Constants for the Cellulose-Dimethyloldihydroxyethyleneurea Reaction

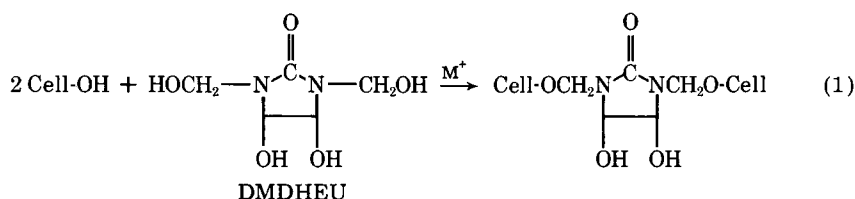
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Synopsis

Rates of the $MgCl_2$ -catalyzed reaction between cellulose and 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone were measured at 70, 90, and 110°C. The rate constants were determined by curing the resin for various times, extracting the unreacted resin, and determining its concentration by liquid chromatography. The energy of activation was calculated from the rate data. This work confirms the pseudo-first-order behavior of this reaction.

INTRODUCTION

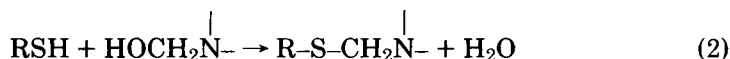
The most important finish applied to cotton fabric is that which imparts durable press characteristics. In 1978, 180 million pounds of durable press resins was consumed, and this is projected¹ to increase to 209 million pounds in 1988. These resins react with cellulose, in the presence of a catalyst and heat, to give a crosslinked polymeric network that exerts restoring forces to smooth wrinkles and retain desired creases.



The dominant resin used for this treatment is 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone (dimethyloldihydroxyethyleneurea, DMDHEU). Reported in this work is a new method for measuring the rates of these reactions. The method involves extraction of the unreacted resin and quantitation by aqueous liquid chromatography.

Previous Rate Studies

Two methods have been used to study the rates of reaction of *N*-methylol reagents and cellulose. Petersen² employed *n*-dodecyl mercaptan as a model for the cellulose nucleophile and measured the rate of production of the substitution product:



This approach gave rate constants for various *N*-methylol and *N*-methoxymethyl compounds, but gave data for a solution reaction which has very different characteristics from the actual crosslinking that takes place heterogeneously in the complex matrix of a cellulosic fiber.

Specific rate constants have been reported by Gonzales and co-workers.³ These rate constants for DMDHEU and a variety of catalysts and temperatures were determined using wrinkle recovery angle, bound nitrogen, and formaldehyde content as measures of reaction progress. All of the aforementioned methods were, however, indirect, in that they measured a result of the crosslinking reaction and did not directly determine a concentration of the resins involved.

With the advent of new analytic procedures⁴ for these durable press agents, it seemed that the rate of the cellulose-DMDHEU reaction might be determined directly by measuring the concentration of the unreacted resin. The analytic method involves aqueous liquid chromatographic (LC) determination of the resin concentration using water as the sole eluent and a column packed with an ion exchange resin. This article reports the results of a study of the rates of the MgCl_2 -catalyzed reaction of DMDHEU with cellulose at three temperatures.

EXPERIMENTAL

Materials

Cotton twill (Testfabrics #445, 190 g/m², bleached and mercerized) was washed with 2.5 g/L AATCC detergent, rinsed thoroughly, and dried. Dihydroxyethyleneurea (DHEU, 4,5-dihydroxy-2-imidazolidinone) was prepared by a literature method.⁵ The DHEU that was reacted with formaldehyde to prepare standard concentrations of DMDHEU was recrystallized from aqueous ethanol. The DHEU used for the preparation of DMDHEU for the pad bath was chromatographically pure (one peak) and used as isolated from the urea-glyoxal reaction (after washing with cold ethanol and drying). Reagent-grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was used as a catalyst.

Calibration Curves

Calibration curves were prepared using a stock solution of 0.50 M DMDHEU. The stock solution was prepared by adding 0.9324 g (11.5 mmol) 37% formaldehyde solution to 5.0 mL (5 mmol) 1.00 M DHEU solution in a 10-mL volumetric flask. Two drops of 5% Na_2CO_3 were added to bring the pH to 8.5 and water added to give 10.0 ml solution that was allowed to stand for 18 h to complete the methylation. (All water used was ultrapure, having been passed through a total deionizing bed, a charcoal filter and a submicron filter.) Aliquots (50, 100, 150, and 200 μL) of this standard solution were diluted to 10.0 ml and analyzed by LC to give the data (peak heights) for the calibration curve. The methylation was complete as evidenced by the absence of monomethylated DHEU (MMDHEU). This method for preparing standard solutions was necessary because it is very difficult to prepare pure crystalline DMDHEU. An excess of formaldehyde was used to ensure complete methylation of DHEU in both the stock solution and in the pad bath.

Pad Bath Preparation

DMEHEU for the pad bath (the solution in which the fabric is immersed) was prepared by adding 7.5 g (92.5 mmol) 37% formaldehyde to 3.579 g (30.3 mmol) DHEU, diluting to 20 mL adjusting the pH to 9.0 with 5% Na₂CO₃, and stirring for 2 h. Before it was used, the solution was checked by LC to be certain that the methylation was complete (no MMDHEU peak). Catalyst (5.0 mL 0.59 M MgCl₂·6H₂O) was added and the volume brought to about 70 mL. The pH was adjusted to 5.0 with 0.05 M HCl and the volume brought to 91 ml to give a solution that was 0.33 M in DMDHEU and 0.033 M in catalyst. The pad bath was acidic to prevent hydrolysis of the DMDHEU to MMDHEU on the fabric.⁶

Fabric Treatment

The fabric sample (18 × 38 cm) was padded (immersed in the pad bath and passed through pressure rolls) with this solution using two dips (immersion in the pad bath) and two nips (passage through the pressure rolls) at an average wet pickup of 91%. This gave an add-on of 5.4%. The wet sample was carefully placed on a horizontal pin frame (to minimize migration due to gravity), dried in a hood, and conditioned (21°C, 65% relative humidity) for 18 h. Free formaldehyde was shown (by extraction and LC analysis) to be present during the drying stage, but was absent in the dried fabric. It is assumed that a small amount of free formaldehyde remained in the fabric, but that it was not large enough to be detected by this analytic technique. The outer edge (1 cm) of the sample was removed and the remaining fabric divided into eight equal pieces. Seven of the pieces were cured by hanging them individually in an oven for a specified period of time at a given temperature (70, 90, or 110°C). The eighth sample was used as a control to determine the total amount of unreacted DMDHEU present prior to curing. A portion (2.5 × 8 cm) of each of the eight samples was milled and conditioned for 18 h.

Fabric Temperature and Weight Loss on Heating

The rate of temperature rise on the fabric surface was determined at each oven temperature (70, 90, and 110°C) by attaching temperature monitoring tape (Tempilabel made by Omega Engineering, Inc.) to the fabric and recording the time (after insertion of the fabric into the oven) at which the spot on the tape turned from white to black. The temperatures were determined in 5 to 6°C increments, depending on the spot, from 43° to 110°C. Times for the fabric to reach oven temperature are: 70°C, 2.14 min; 90°C, 2.08 min; 110°C, 1.92 min. These times are independently useful at the stipulated temperatures, but cannot be compared across temperatures because of the different heat fluxes involved.

The weight loss on heating (as a percent of the original conditioned weight) was determined by inserting the weighed fabrics, after padding, drying, and conditioning, into the oven for specified times and then weighing immediately after removal from the oven. For example, the weight loss at 90°C reached a maximum of 6.8% after 2.0 min, leaving less than 1% moisture in the fabric. Nearly all of the kinetic data points for this temperature were taken after 2.0 min.

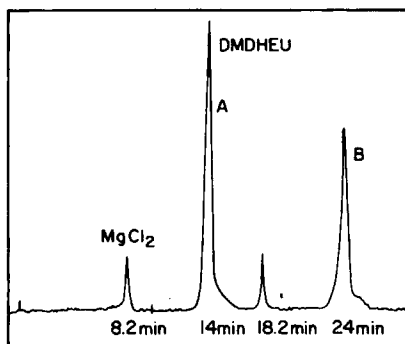


Fig. 1. Chromatograms of $MgCl_2$ and DMDHEU from (A) uncured and (B) 14-min cure at 90° . (Sample B injected 10 min after sample A.)

With such a small amount of water present in the fibers, little or no migration of resin or catalyst should be possible during heating.

Analytic Procedure

Each milled sample was then analyzed for unreacted DMDHEU by LC. The fiber sample (ca. 200 mg) was accurately weighed into a 15-mL medium-porosity fritted glass funnel. Water (4.5 mL) was pipetted into the funnel and the sample stirred occasionally with a glass stirring rod. After 2 min, suction was applied and the liquid collected in a 25-mL suction flask. The vacuum was released, the fibers were washed with 2.0 mL water, and suction was again applied. A second 1.0-mL wash was given to the fibers and the total filtrate transferred quantitatively to a 10.0-mL volumetric flask. The volume was brought to 10.0 mL and the sample analyzed directly by LC. The chromatograms of the extracts of uncured and 14-min cured samples at 90° are shown in Figure 1. Note that sample injections can be made every 10 min without interfering with the separation. The small shoulder on peak B is MMDHEU. When it appeared, it was less than 1.5% of the DMDHEU peak. Peak heights were measured manually and converted to concentration (mmol/mL) by dividing by the slope of the calibration curve (Fig. 2) that was run immediately after the analysis of the eight samples for a given cure temperature. The correlation coefficients for all calibration curves were at least 0.999. In all cases, linear regression was used to determine the slope of the best line.

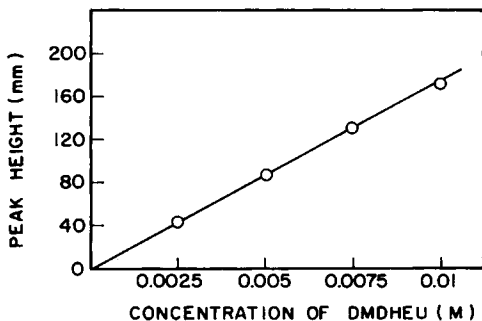


Fig. 2. Calibration curve for DMDHEU.

Column Conditions

The column used for the analyses was 8 mm × 410 mm and packed as previously reported⁴ with the lithium form of Aminex Q-15S cation exchange resin. At a flow rate of 0.7 mL/min, the retention times (as determined by injection of authentic samples) of DMDHEU, MMDHEU, DHEU, and formaldehyde were 14.0, 15.1, 16.6 and 17.8 min, respectively.

RESULTS AND DISCUSSION

Several experiments were run to determine the accuracy and precision of this approach for measuring rates of this etherification reaction with cellulose. (1) To determine the uniformity of the finish applications, a sample (18 × 38 cm) of fabric was padded, dried, and conditioned. The fabric was sampled a total of 11 times across its width and length and showed a coefficient of variation (CV) of less than 2% for the concentration of DMDHEU. (2) To ascertain the reproducibility of the LC method, the same extract was injected several times, giving a CV of less than 0.6%. (3) To check the reproducibility of the extraction procedures, duplicate samples of the same partially cured fabric were analyzed and showed a CV of less than 0.6% for the amount of extracted DMDHEU. (4) To prove that the unreacted DMDHEU is quantitatively transferred from the fibers to the water, the extracted fibers of several samples were reextracted. The filtrates showed no DMDHEU by LC. These results indicate that the described method for measuring the concentration of unreacted DMDHEU is both accurate and precise.

The raw data from the LC analyses were treated in the following manner to arrive at the various rate constants:

$$\frac{\text{PH} \times 10}{\text{slope} \times \text{sample wt}} = \frac{\text{mmol DMDHEU}}{\text{mg cell-OH}} \quad (3)$$

The quotient of peak height (PH) divided by slope gives concentration in mmol/ml. Multiplying this by 10 ml (sample volume) and dividing by the sample weight gives a concentration of resin per mg cellulose. A plot of this quantity vs. time for the 110°C cure is shown in Figure 3. From this figure it can be concluded that the etherification reaction began at about 0.7 min. This is now taken as time zero (t_0) and the other times adjusted accordingly, i.e., by subtracting 0.7 from each point after the start of the reaction.

This temperature-dependent induction period seems justifiable in two ways. (1) The initial rate of rise of fabric temperature parallels the rate of weight loss on heating. The fiber temperature will not rise rapidly till the water is evaporated from the fabric. Therefore, it takes a finite period of time to drive out most of the water and to begin to cause the fiber temperature to rise. (2) Petersen², in his model studies, showed that significant concentrations of the intermediate carbonium-immonium ion are generated only after an induction period. It therefore seems reasonable to invoke an induction period in these calculations. From Figure 3, it may be noted that the point at 0.5 min shows a higher value for DMDHEU concentration on fabric than the control. This point was reproducible but was observed only in the 110° cure. Certain causes for this abnormal behavior were ruled out. The initial concentration of DMDHEU was measured in each kinetic run and the ratio of DMDHEU/cellulose remained quite constant

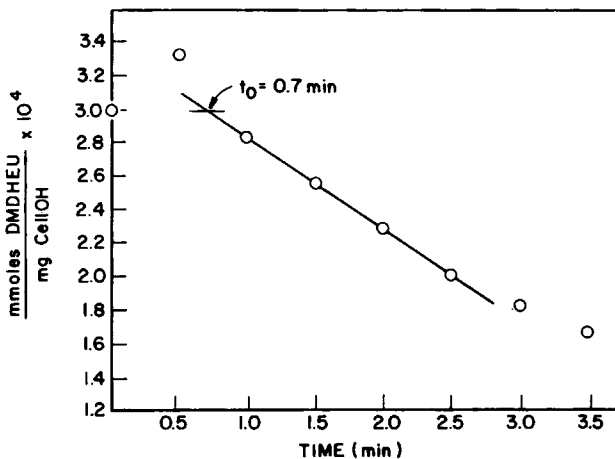


Fig. 3. Concentration of unreacted DMDHEU vs. time at 110°C.

from run to run. Since there was no other source of DMDHEU to cause an increase in the numerator, the only possible explanation for the anomalous point is a decrease in the weight of cellulose in the denominator. The temperature of the fabric at 0.5 min was about 60°C, considerably below the point at which $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ loses two water molecules (100°C) or begins to liberate HCl (110°C).⁷ Since the sample was conditioned after heating and then weighed before extraction, the high value for A at 0.5 min in Figure 3 cannot be rationalized as a loss of moisture during heating. Also, there is no detectable formaldehyde in the dry fabric, so loss of formaldehyde should be ruled out as a cause for the increase in A . Therefore, this temperature-dependent anomalous behavior remains unexplained.

If this etherification reaction is pseudo-first order, eq. (4), and its rate is dependent only on the resin concentration, a plot of $\ln(A_0/A)$ vs. t should give a straight line with a slope equal to the rate constant k . In this case A_0 is the concentration of DMDHEU at t_0 and A is the concentration at time t :

$$\ln A_0/A = kt \quad (4)$$

Such a plot is shown in Figure 4 for the 110°C cure. The correlation coefficient for this line is 0.9996 and the slope (k) is 0.212 min^{-1} .

Repeating the cures at 90° and 70°C gives results that are shown in Table I.

Since $-R \ln k = E_a(1/T)$, a plot of $\ln k$ vs. $1/T$ (K) should give a line with a slope of $-E_a/R$. Figure 5 shows the graph of the data in Table I. The resulting energy of activation is 29.2 kcal/mol and compares very favorably with the value of 29.4 kcal/mol reported previously.³ The correlation coefficient for the line in Figure 5 is 0.995.

These data confirm the results of the previous studies³ that showed the DMDHEU-cellulose reaction to be pseudo-first order in the resin. In a pseudo-first-order reaction, neither the catalyst nor the substrate concentration should change. The catalyst concentration, as indicated by the ratio of the peak height of MgCl_2 to the sample weight, remains constant throughout the curing process. If the DP of cellulose is assumed to be 2000, then there are 2000 hy-

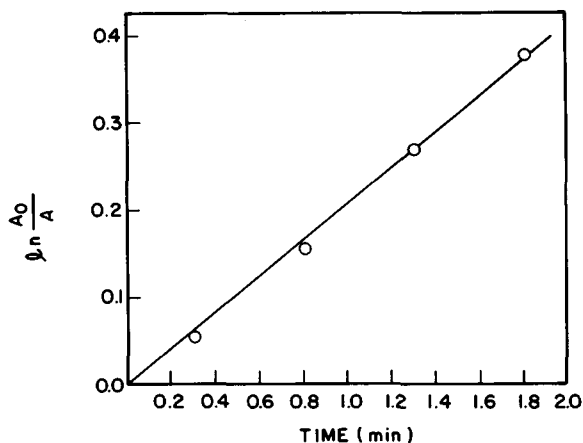


Fig. 4. First-order plot for Cell-OH + DMDHEU at 110°C. Slope (k) = 0.212 min⁻¹.

droxyl groups on C-6 available for etherification by DMDHEU. There would also be the same number of available hydroxyl groups at C-2 and C-3, but these are far less reactive than the 6-OH.⁸ For every 100 g (3.1×10^{-4} mol) of fabric (cellulose) there would be 5.4 g (3.0×10^{-2} mol) of DMDHEU, for a 5.4% resin add-on. In the hypothetical 100-g sample of cellulose, 0.62 mol ($2000 \times 3.1 \times 10^{-4}$ mol) of 6-OH would be available for crosslinking. At 20% reaction, 6.0×10^{-3} mol ($3.0 \times 10^{-2} \times 0.2$) of DMDHEU would react with 13.6×10^{-3} mol ($6.8 \times 10^{-3} \times 2$) of 6-OH for a change of 2.2% in the number of available 6-hydroxyls. This is an example of the worst case where resin reacts only with 6-OH. In practice, certainly some of the resin will react with 2-OH or 3-OH, making the percent change in available hydroxyl groups of anyone type lower than the 2.2%. In this case, then, it can be assumed that the hydroxyl concentration remains essentially constant and that the reaction is pseudo-first order in the resin.

CONCLUSIONS

Extraction and liquid-chromatographic determination of unreacted DMDHEU as a direct means of measuring the rate of the cellulose-DMDHEU reaction has been shown to be accurate, precise, relatively rapid, and simple. For the MgCl₂-catalyzed reaction between DMDHEU and cellulose, rate constants were measured at cure temperatures of 70, 90, and 110°C and the reaction shown to follow pseudo-first-order kinetics. It is interesting to note that the rate constant decreases by a factor of about 5 as the temperature was decreased from 110° to 90°C but the change from 90° to 70°C caused the rate to drop by a factor of 15. The energy of activation calculated from an Arrhenius plot was 29.2 kcal/mol.

TABLE I
Rate Constants for MgCl₂-Catalyzed Cellulose-DMDHEU Reaction

Temp., °C	k , min ⁻¹ × 10 ³
70	2.64
90	40.5
110	212

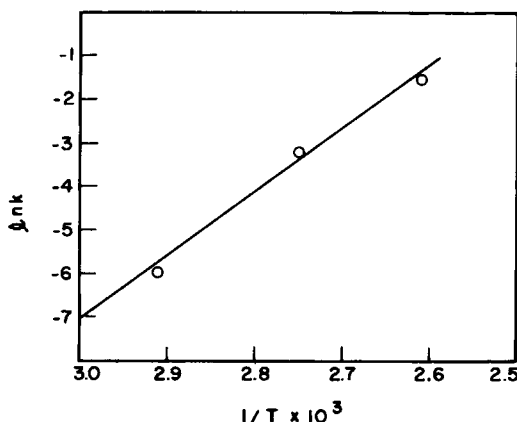


Fig. 5. Arrhenius plot for MgCl_2 -catalyzed DMDHEU—Cell-OH reaction.

This method for obtaining kinetic and thermodynamic parameters should prove very useful in the study of other reactions of this type.

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