

Influence of Structure of Cyclic Urea Derivatives on Their Reactivities with Cotton

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Synopsis

The structure of the cyclic urea influenced the rate of reaction with cotton cellulose and the mechanism by which reaction occurred. Reaction of *N,N'*-dimethylolethyleneurea (DMEU) and *N,N'*-dimethylolpropyleneurea (DMPU) with cellulose in presence of inorganic salt catalysts proceeded through methylol hydroxyls and at the same rate; but reaction mechanism differed. With DMEU, $N \rightarrow$ metal ion coordination occurred and S_N2 mechanism prevailed. With DMPU, $O \rightarrow$ metal ion coordination resulted.

Reaction of dihydroxyethylene urea (DHEU), *N,N'*-dimethyldihydroxyethyleneurea (DMeDHEU), and *N,N'*-dimethyloldihydroxyethyleneurea (DMDHEU) with cotton cellulose proceeded through ring hydroxyls with the formation of a carbonium ion, indicating an S_N1 mechanism. The much faster rate of reaction with DMeDHEU than with DHEU was attributed to the more electronegative environment of its ring hydroxyl, while the much slower rate of reaction of DMDHEU was attributed to hydrogen bonding between its methylol and ring hydroxyls.

INTRODUCTION

Cyclic urea derivatives used in chemical modification of cotton cellulose have been studied at this laboratory¹⁻⁷ and by Petersen and coworkers⁸⁻¹⁰ to determine their effects upon physical and chemical properties of cotton and the kinetics of their reactions with cotton. In earlier papers,¹⁷ emphasis was on the influence of the metal ion catalyst upon the physical properties of the finished cottons and upon the activation parameters for the various cellulose-cyclic urea reactions. The present study is concerned with the influence of structural changes of the cyclic urea upon physical and chemical properties of cotton fabrics reacted at high temperature of cure in the presence of an active catalyst and upon the kinetics and activation parameters of the cotton-cyclic urea reaction. The importance of such data is emphasized by the recent utilization of kinetic data by Ruttiger¹¹ in the development of an analog computer designed such that resin finishing formulations and process data for the chemical finishing of cotton can be easily determined.

EXPERIMENTAL

Materials

Cyclic urea derivatives, prepared as published previously,¹⁻⁷ included (1) *N,N'*-dimethylolethyleneurea (DMEU); (2) *N,N'*-dimethyloldihydroxyethyleneurea (DMDHEU); (3) dihydroxyethyleneurea (DHEU); (4) *N,N'*-dimethylolpropyleneurea (DMPU); and (5) *N,N'*-dimethyloldihydroxyethyleneurea (DMeDHEU). Purity of recrystallized products,

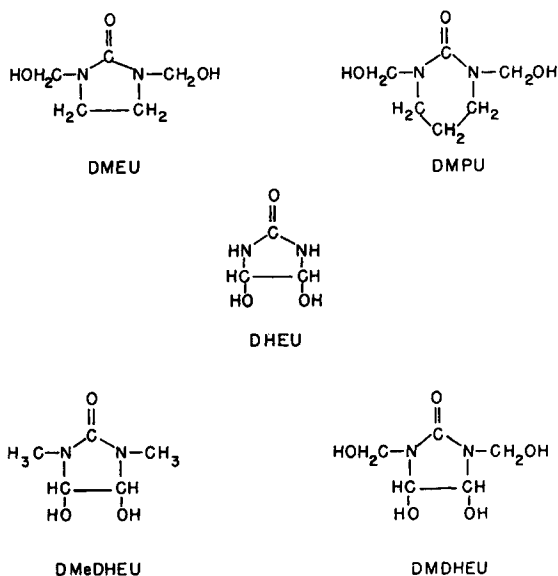


Fig. 1. Formulas and abbreviations of substituted cyclic ureas.

whose structural formulas are given in Figure 1, was in all cases greater than 98%.

Inorganic salt catalysts were of analytical grade. Fabric specimens were from 80 × 80 cotton print cloth which weighed 3.2 oz/sq yd and which had been desized, scoured, and bleached.

Procedure

(A) High temperature curing studies were performed on fabrics which had been twice-padded to 100% wet pickup with solutions 0.55 *M* with respect to urea reactant and 0.03 *M* with respect to catalyst. Fabrics were dried for 7 min at 60°C, cured for 3 min at 160°C, given a mild after-wash, and then tumble dried. Fabrics were air-equilibrated for 16 hr and then tested for physical and chemical properties which included breaking strength,^{12a} wrinkle recovery angles,^{12b,13} nitrogen content by Kjeldahl method, formaldehyde analysis by chromotropic acid method,¹⁴ metal analyses by ashing of metal oxides and by X-ray fluorescence¹⁵ and infrared spectra by the KBr disk technique.¹⁶

(B) For kinetic studies, only the drying step was eliminated, and a lower curing temperature was used so that specific reaction rate constants could be measured.¹ After selected times of reaction at the lower temperatures, fabrics were removed, rinsed in hot tap water (pH = 10) for 15 min, and allowed to line dry for 16 hr before being tested. Curing temperatures ranged from 45 to 85°C, depending upon the reactivity of the cyclic urea derivative with cotton. Fabrics were reacted with each cyclic urea in the presence of each of four metal ion catalysts—Zn(NO₃)₂, ZnCl₂, Mg(NO₂)₂, and MgCl₂.

RESULTS AND DISCUSSION

High Temperature Cure

Since earlier work¹⁻⁷ showed Zn(NO₃)₂ to be the most effective catalyst, it was used for the studies at high (160°C) temperature of cure. It should be pointed out, however, that efficiency of the cyclic urea derivative in producing certain levels of physical and chemical properties in finished cottons varied with the catalyst, the catalyst to anhydroglucose mole ratio, and the mole ratio of catalyst to cyclic urea reactant.¹⁻⁷ Rüttiger¹¹ demonstrated that catalysts can have different threshold values for promoting reaction between cotton and the cyclic urea. Figure 2 shows the effect of molarity of Zn(NO₃)₂ on nitrogen content and on conditioned wrinkle recovery of cotton finished with each of the cyclic ureas. With the exception of DMEU, the nitrogen content of treated fabrics passed through a minimum at 0.03 M catalyst concentration. At that concentration, the conditioned

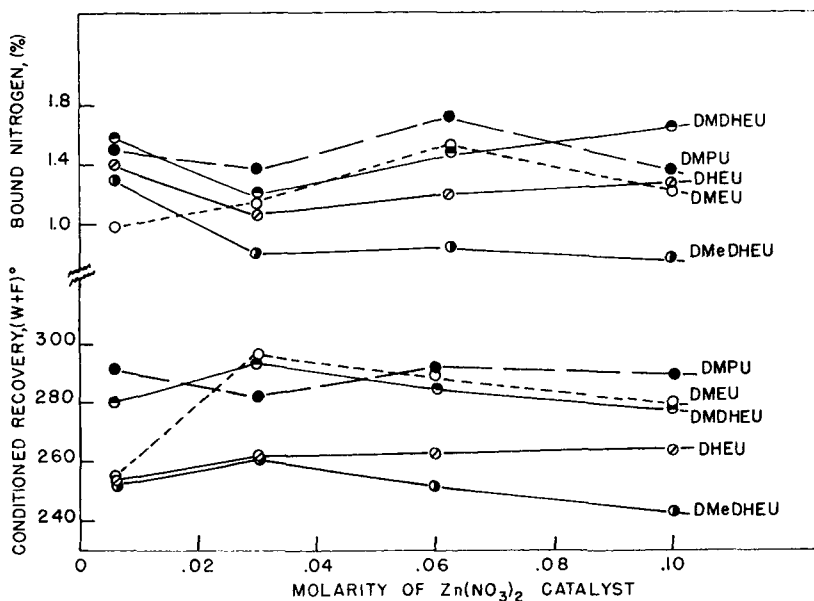


Fig. 2. Variation of conditioned recovery angles and of bound nitrogen with molarity of Zn(NO₃)₂ used to catalyze the reaction of cotton with 0.55 M urea derivative.

TABLE I
Effect of Cyclic Urea Derivative on Fabric Properties^a

Reactant	Nitrogen %	Formal- dehyde, %	Equiv- alent ratio N/Form.	Recovery angles (W + F) ^o		Breaking strength % retained
				Condi- tioned	Wet	
DMEU	1.0	2.20	1.0	296	270	48
DMDHEU	1.1	1.85	1.3	293	289	48
DMPU	1.4	2.37	1.2	282	266	69
DHEU	1.1	—	—	261	242	57
DMeDHEU	0.8	—	—	261	240	64
Control	—	—	—	190	150	(50 lb)

^a 80 × 80 cotton print cloth twice padded to 100% wet pickup with aqueous 0.55 *M* urea derivative and 0.03 *M* Zn(NO₃)₂, dried 7 min at 60°C, and cured for 3 min at 160°C.

wrinkle recovery of all except that fabric treated with DMPU reached a maximum. Nitrogen contents and wrinkle recovery angles of fabrics treated with DMEU, DMDHEU, or DMPU (group *A*) were higher than those of cottons treated with DHEU and DMeDHEU (group *B*). Group *B* ureas possessed only ring hydroxyls for reaction, whereas those in group *A* possessed methylol hydroxyls only or methylol and ring hydroxyls.

Effects of structural changes in cyclic urea reactants upon some physical and chemical properties of cottons finished at 160°C can be seen in Table I. All specimens possessed greatly improved dry and wet recovery angles. With the exception of fabric treated with DMDHEU, wet recovery angles were significantly lower than dry. With DMDHEU, the improvement in wet recovery was about 40° higher than the improvement in dry recovery; with the others, improvement in wet exceeded improvement in dry by only 20(W + F)^o. Enlargement to a six-membered ring (DMPU vs. DMEU) resulted in significant increases in nitrogen contents and breaking strength retention, and only slight reduction in dry angles (12 degrees is considered significant). The presence of ring hydroxyls on the five-membered ring of DMEU (DMDHEU vs. DMEU) had little or no effect upon nitrogen content, breaking strength retention, or dry recovery angle, but caused an increase in wet recoveries and a decrease in formaldehyde content. From these data on group *A*, one might attribute higher wet recovery obtained with DMDHEU to presence of ring hydroxyls or to reaction of cotton with both methylol and ring hydroxyls. Apparently, ring hydroxyls in addition to methylol hydroxyls caused no further improvement in dry recovery. Fabrics treated with group *B* reagents differed from each other in nitrogen contents and breaking strength retentions. Recovery angles were apparently independent of nitrogen substituent. Lower wet and dry recovery angles resulted when cotton was reacted with ureas having ring hydroxyls only than with ureas containing methylol hydroxyls.

Nitrogen to formaldehyde equivalent ratios (N/HCHO) were computed from percentages of N and HCHO remaining in treated fabrics and are

defined as 2.14 (%N/%HCHO) where 2.14 is the ratio of equivalent weights of HCHO to N in cyclic urea molecules. Within experimental error, the ratios were approximately equal for the DMPU and DMDHEU reaction products and were somewhat higher than that of the DMEU reaction product. The ratio of 1.0 for DMEU-treated cotton indicated presence primarily of monomeric crosslinks. Ratios greater than 1.0 for DMPU and DMDHEU indicated presence of polymeric crosslinks.

Low Temperature Cures

In the temperature range of 45° to 85°C, rates of reaction between cotton and each urea derivative could be differentiated with each of the four catalysts. Although relative rates differed with each catalyst, the order of reactivity was always DMEU \geq DMPU > DMeDHEU \gg DHEU \geq DMDHEU. Inclusion of an additional carbon atom in the urea ring did not greatly affect the rate of reaction; but the presence of only ring hydroxyls or of ring hydroxyls together with methylol hydroxyls did result in a slower rate of reaction.

Activation parameters for each of the cellulose—cyclic urea reactions were determined over the temperature range of 45° to 85°C. Enthalpies (ΔH^*), entropies (ΔS^*), and free energies (ΔG^*) at 45°C for the $Zn(NO_3)_2$ catalyzed reaction based on percent bound nitrogen are recorded in Table II. Free energies of activation varied from 25.3 to 28.2 kcal/mole; and in

TABLE II
Activation Parameters at 45°C of the Cotton-Cyclic Urea
Derivative Reactions in the Presence of 0.03 M $Zn(NO_3)_2$
(Based on Percent Nitrogen)

	ΔH^* (kcal/mole)	ΔS^* (cal/mole°)	ΔF^* (kcal/mole)
DMEU	4.0	-66.8	25.3
DMDHEU	43.3	47.5	28.2
DMPU	25.6	0.7	25.4
DHEU	34.9	22.3	27.8
DMeDHEU	35.9	31.2	26.0

order of increasing ΔG^* the urea derivatives ranked as follows: DMEU = DMPU < DMeDHEU < DHEU \leq DMDHEU. Although ΔG^* values for DMEU and DMPU were equal, changes in ΔH^* and ΔS^* for these two cellulose-urea derivatives indicated differences in energy absorbed in the formation of the transition state complex and in the degree of order of the activated complex. The large negative ΔS^* for DMEU reaction indicated that the transition state complex was more ordered than the initial state and that the reaction proceeded by an S_N2 mechanism. The essentially zero ΔS^* with DMPU, showing no difference in order of the activated and initial states of reactants, indicated that the mechanism for this reaction differed from that for cellulose-DMEU.

Although ΔG^* values for DHEU and DMDHEU reactions with cotton

were essentially equal, their ΔH^* and ΔS^* values were different. Large positive ΔS^* values for DHEU, DMDHEU, and DMeDHEU indicated that activated complexes were less ordered than initial states of reactants. The largest positive ΔS^* —associated with the cellulose-DMDHEU reaction—indicated that compared to original reagents the transition state complex of this reagent was most disordered. The largest ΔH^* , also associated with this reaction, indicated the greatest amount of energy absorbed in the formation of this activated complex. Variations of ΔS^* from a large negative value for DMEU to zero for DMPU to large positive values for DHEU and its substituted derivatives indicated different mechanisms for their reactions with cellulose.

Infrared Data

Table III contains wave numbers (cm^{-1}) of four characteristic infrared

TABLE III
Characteristic Infrared Absorption Bands of Cyclic Urea
Derivatives and Their Cotton Cellulose Products

IR absorption Compound	Crystalline cyclic ureas				C=O out of plane bending
	C=O Amide I	C—N Amide II	N—C—N		
	Frequency in cm^{-1}				
DMEU	1672	1504	1458		772
DMPU	1626	1524	1458		764
DHEU	1672	1493	1466		763
DMDHEU	1709	1504	—		772
DMeDHEU	1666	1504	1456		764
EU	1660	1502	1445		767
PU	1686	1540	1443		760

Treatment ^b	Cellulose-cyclic urea products ^a				Absorbed H ₂ O
					+ = present - = absent
DMEU (U)	1680	1504	1458	—	—
DMEU (Z)	1698	1504–1482	1458–1449	764	—
DMPU (U)	1631	1520 (sh) ^b	1460	—	—
DMPU (Z)	1631	1518	1504	752	—
DHEU (U)	1718	—	—	—	+
DHEU (Z)	1718	—	—	—	+
DMDHEU (U)	1709	—	—	—	+
DMDHEU (Z)	1718	1497 (sh)	—	—	—
DMeDHEU (U)	1703	—	—	—	+
DMeDHEU (Z)	1703	—	1456 (sh)	—	—

^a 80 × 80 Cotton print cloth twice padded to 100% wet pickup with aqueous 0.55 M derivative, dried 7 min at 60°C and cured for 3 min at 160°C.

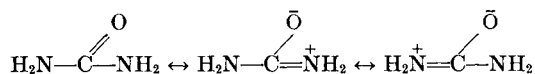
^b U = Uncatalyzed reaction product; Z = Catalyzed reaction product. Catalyst = 0.03 M Zn(NO₃)₂, sh = shoulder.

absorptions associated with stretchings of the carbonyl, C—N, N—C—N, and C=O out of plane bending of the various cyclic ureas and of their cellulosic products. The products are those obtained with $Zn(NO_3)_2$ at the 160°C cure temperatures. Absence or presence of the adsorbed water band of native cotton cellulose (6.1 μ) in finished products is also indicated.

Ureas

Comparison of absorptions for crystalline reactants showed the position of the C=O stretching absorption to be the same for DMEU and DHEU and to be at slightly higher frequency than that of the parent compound, ethyleneurea (EU). Thus methylation or presence of ring hydroxyls alone increased the double bond character of the C=O bond to the same extent. With DMDHEU, where both methylol and ring hydroxyls were present, shift of the carbonyl band to an even higher frequency indicated a carbonyl bond with stronger double bond character than in either DMEU or DHEU crystals. Hydrogen bonding between the methylol and ring hydroxyls in DMDHEU would stabilize the ring structures and account for increased double bond character of the carbonyl group and for almost complete absence of the N—C—N vibration found at 1466 cm^{-1} (6.83 μ) in the spectra of DHEU. Substitution on the N atom of the electron releasing group, CH_3 , as in DMEDHEU, resulted in a shift of the C=O band to slightly higher frequency than that observed in EU but lower than that observed with DMEU, DHEU, and DMDHEU.

A further lowering in C=O frequency, when size of the ring was increased to a six-membered ring by inclusion of an additional carbon atom, indicated less double bond character in DMPU than that in ethylene urea or its derivatives. It is known that urea is a resonance hybrid of the following canonical structures:



Physical chemical data for urea¹⁷ have shown that the C—O bond is not

100% double in character, but exists as 40% $\begin{array}{c} O \\ || \\ -C-N \\ \diagup \quad \diagdown \end{array}$ and 60% $\begin{array}{c} O^- \\ | \\ -C=N^+ \\ \diagup \quad \diagdown \end{array}$.

A carbonyl linkage of strong double bond character (high wave number) is responsible for a high electron density at the nitrogen atom and is synonymous with less resonance energy in the urea derivative. A decrease in strength of the carbonyl double bond (low wave number) indicates a low electron density at the nitrogen atom, a large resonance stabilization

energy, or a large contribution of the $\begin{array}{c} O^- \\ | \\ -C=N^+ \\ \diagup \quad \diagdown \end{array}$ structure to the resonance

energy. The wave number of the C=O group in propylene urea (PU), where there is less strain than in the planar EU ring, is not too different

from that of urea (U), indicating that the C=O character is about the same for both reagents. However, methylation of PU resulted in a

carbonyl of less C=O character; or the percentage of the $\text{—C}=\overset{\text{O}}{\overset{+}{\text{N}}}$ character is greatly increased. In DMPU, H-bonding between an N-methylol group and the carbonyl oxygen helps to stabilize the mesomeric

activity or contribution of the $\text{—C}=\overset{\text{O}^-}{\overset{+}{\text{N}}}$ structure. In contrast, due to

the planarity of the EU ring, H-bonding between the carbonyl oxygen and the N-methylol groups of DMEU is unlikely and the electrons of the nitrogen cannot easily mesomerize with those of the carbonyl oxygen. Therefore, methylation of EU to DMEU results in a compound with only a little more C=O character than the original EU. Substitution of ring hydroxyls in EU, as in DHEU, has the same effect on the C=O frequency as does substitution of N-methylol groups. However, when both ring and N-methylol groups are present, as in DMDHEU, intra H-bonding between

these unlike hydroxyl groups stabilizes the compound in the $\text{—C}=\overset{\text{O}}{\overset{-}{\text{N}}}$ structure and results in the compound with greatest C=O character. Thus, DMDHEU should have the greatest electron density on its nitrogen atoms and DMPU should have the most electropositive nitrogen and greatest stabilization by resonance energy of this series. Based on observed carbonyl absorption bands, the pure urea derivatives have the following order when ranked from highest to lowest electron density at the N atom:



Nuclear magnetic resonance spectra¹⁸ provided information on environments of protons of ring and methylol hydroxyls of these cyclic urea derivatives in deuterated dimethylsulfoxide at 35°C. Table IV gives the position of proton resonance in Hz downfield from tetramethylsilane internal standard for methylol and ring hydroxyl protons for the ureas investigated. DMDHEU, which possessed the greatest degree of C=O character, had an NMR spectrum showing a broad band for the methylol proton and showing it to be in the most negative environment. This was due to the methylol hydroxyl acting as donor in the formation of intra-H-bond with the oxygens of ring hydroxyls of the DMDHEU molecule. The electron density of environments of the protons of the methylol groups was DMDHEU > DMEU > DMPU, and the order correlated with the decrease in C=O character of these compounds as determined by IR. However, two proton signals were associated with resonance of methylol hydroxyls of DMPU indicating that protons on its two methylol groups were not equivalent. Compounds possessing ring hydroxyls—DHEU, DMDHEU, and DMe-

TABLE IV
Pertinent Spectral Data for Cyclic Urea Derivatives

Reagent	Wave no. ^a C=O cm ⁻¹	Proton signals ^b	
		Methylol hydroxyl Hz	Ring hydroxyl Hz
EU	1660	—	—
DMEU	1672	335	—
DHEU	1672	—	353
DMDHEU	1709	343 br ^c	343 br
DMeDHEU	1666	—	365
PU	1686	—	—
DMPU	1626	{ 324 323	—

^a IR data.

^b NMR data (ref. 18). Spectra taken at 35°C in deuterated dimethylsulfoxide; position as shown as Hz downfield from tetramethylsilane internal standard.

^c br = broad.

DHEU—are *trans* isomers and NMR data indicated that electron environments of the proton on the ring hydroxyls of each of these reagents differed. The hydroxyl proton on DMeDHEU resonated farthest downfield, showing it was in the most negative environment. The proton signal shift was least for the proton of the ring hydroxyl of DMDHEU; and, hence, of these three compounds, it possessed the least negative environment. Although the C=O wave number of DMEU and of DHEU was the same (1672 cm⁻¹), the ring hydroxyl proton of DHEU resonated farther downfield than did the methylol proton of DMEU. Consider that portion of

the structure, $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—N—C—OH} \\ | \quad | \\ \quad \quad \text{B} \end{array}$ in both DMEU and DHEU. In DMEU,

A = B = H; whereas A = H but B is a carbon in DHEU. Therefore the proton in DHEU is in an environment of greater electron density. Simi-

larly, although the C absorption of DMeDHEU is at 1666 cm⁻¹ rather than at 1672 cm⁻¹ as in DHEU, its proton is in an environment of the greatest electron density because of the substitution of the electron releasing group on the nitrogen. The protons of the ring hydroxyls of DMDHEU are in an environment of less electron density than those in DHEU because of the intra-H-bonding in the former.

It has been noted earlier that the order of reactivity of these cyclic ureas with cotton was: DMEU ≥ DMPU > DMeDHEU ≫ DHEU ≥ DMDHEU. Consideration of this order of reactivity in light of electron densities of environments of protons of methylol hydroxyls of DMEU, DMPU, and DMDHEU indicates that as electron density increased the

rate of reaction decreased. A similar consideration of order of reactivity in light of electron densities of environment of protons of ring hydroxyls of DMDHEU, DMeDHEU, and DHEU showed that the molecule with the greatest electron density (DMeDHEU) reacted the fastest. DHEU, with same degree of C=O character as DMeDHEU (based on IR), reacted more readily with cotton than did DMDHEU, the molecule with the strongest

C=O character. These facts show that the $\text{—C}=\overset{\text{O}^-}{\overset{+}{\text{N}}}$ structure does not

greatly influence the rate of reaction of each of these three compounds with cotton and that reaction proceeds through their ring hydroxyls. When compared to DMEU and DMPU, the much slower reaction of DMDHEU with cotton is probably due to the fact that methylol hydroxyls act as proton donors in hydrogen bonding with oxygens of ring hydroxyls as acceptors and that reaction with cotton occurs through the ring hydroxyls rather than through methylol hydroxyls. Data indicate that only DMEU and DMPU reacted through methylol groups but by different mechanisms. DMEU, which had a large negative ΔS^* and a small ΔH^* of activation (Table II) with cotton, had free rotation of methylol groups about the N—C bond and the higher degree of C=O character. While DMPU reacted at about the same rate as DMEU, its reaction with cotton was enthalpy controlled, as it had a negligible ΔS^* . NMR and IR data indicated that DMPU had restricted rotation of the methylol groups about the N—C bond and a higher degree of C—O single bond character for the carbonyl bond. These data, considered in conjunction with molecular models, indicated that DMPU had two intra-H-bonds with the methylol group acting as donor and the carbonyl oxygen and one nitrogen as acceptors.

Cellulose Products

In the finished cotton products, the C=O wave number was approximately 1700 cm^{-1} for all EU derivatives and only 1631 cm^{-1} for the cotton finished with DMPU. This would indicate stabilization of the urea group

in a $\text{—C}=\overset{\text{O}}{\text{N}}$ configuration in those resins having the planar five-membered ring and stabilization in the $\text{—C}=\overset{\text{O}^-}{\overset{+}{\text{N}}}$ configuration in the product

having the six-membered ring where the electrons of the carbonyl O and amide N mesomerize to stabilize the product through its resonance energy.

Reaction with cellulose resulted in significant increases in the carbonyl absorption frequencies of DMEU, DHEU, or DMeDHEU. With the latter two containing only ring hydroxyls, the increase occurred even in the absence of the salt catalyst. In the cotton-DMEU product, the increase in frequency of the C=O band was greater in the presence than in the

absence of catalyst. With DMPU and DMDHEU, the C=O stretching vibration was not significantly affected after reaction with cotton.

In the cellulose-DMEU products formed with $Zn(NO_3)_2$ catalyst, shifts to lower frequencies of bands associated with C—N and N—C—N vibrations accompanied shifts to higher frequencies of the C=O band, and a weak absorption appeared at 13.1μ (764 cm^{-1}). These shifts in C—N and N—C—N absorptions indicated more single bond character of the carbon-nitrogen bond. The band at 13.1μ was attributed to C=O out of plane bending; and its appearance in addition to the above frequency shifts was interpreted as indicating N \rightarrow metal bonding in the formation of a metal ion complex with DMEU. The adsorbed water band of native cellulose (6.1μ) was absent from the spectra and activation parameters indicated an S_N2 mechanism.² It should be noted that EU forms metal ion complexes with Zn^{++} ions via carbonyl O \rightarrow metal bonding.¹⁹ However, in the cotton-DMEU reaction product, spectral data indicated N \rightarrow metal bonding in line with the more electronegative N in the cotton-DMEU product and a more electronegative O in EU.

IR spectra of cellulose-DMPU products indicated that this reaction differed from that of cellulose-DMEU reaction, thereby confirming conclusions based on activation parameters. Spectra of DMPU crystals showed strong absorptions at 1626, 1524, 1458, 763, 709 cm^{-1} , attributed to C=O stretching, C—N, N—C—N, C=O out of plane bending and N—CH₂ rocking, respectively. Spectra of cellulose reaction products showed no significant shift in the strong C=O absorption; and intensities of absorptions due to C—N, N—C—N, and N—CH₂ rocking were reduced significantly. Only when $Zn(NO_3)_2$ catalyzed the reaction was there an indication of a weak absorption at 13.1μ , showing some slight influence of the metal ion upon the C=O out of plane bending of the DMPU ring. The presence or absence of the adsorbed water band was masked by the carbonyl absorption.

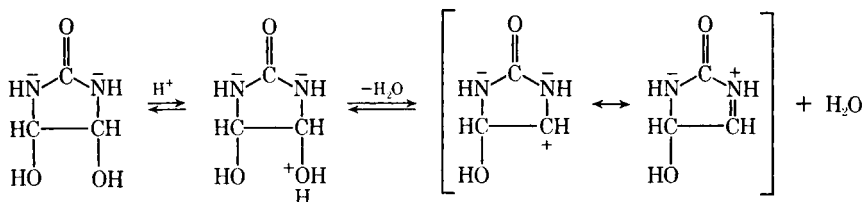
In cellulose reaction products with DHEU and DMeDHEU, reagents possessing only ring hydroxyl reaction sites, shifts in C=O stretching to higher frequencies were noted even in absence of the metal salt catalyst and were identical to carbonyl shifts in the presence of $Zn(NO_3)_2$. Bands attributed to C—N, N—C—N, and C=O out of plane bending vibrations in the crystalline compounds were virtually absent from spectra of DHEU- and DMeDHEU-cellulosic products. Unlike spectra of cellulosic products from DMEU and DMPU, however, absorption spectra from DHEU- and DMeDHEU-reaction products still showed evidence of the adsorbed water band of native cotton cellulose although its intensity was greatly reduced.

After DMDHEU-cellulose reactions, the carbonyl stretching absorption was unaffected even in presence of $Zn(NO_3)_2$ catalyst; and absorptions attributed to C—N and C=O out of plane bending in spectra of crystalline DMDHEU were no longer evident in spectra of cellulosic products. The absorbed water band occurring in native cotton cellulose at 6.1μ was present as a weak absorption with uncatalyzed DMDHEU-cellulose products but was almost completely absent from $Zn(NO_3)_2$ catalyzed products.

Proposed Mechanisms

Petersen^{9,10} has reported on the crosslinking of cotton with these compounds in light of the hydrolyses of both the methylol compounds and the alkoxymethyl compounds resulting from the various crosslinking reactions. He has also¹⁰ considered equilibria of the various N-methylolated ureas and the nucleophilic substitution reactions in light of the electron density at the nitrogen atom* as indicated by IR data. According to Petersen,⁹ structural factors affecting reactivity of N-methylol compounds in acid media included (1) electron density at the nitrogen atom; (2) ability of carbonyl group to coordinate protons; (3) presence of basic centers in the molecule; (4) presence of substituents which cause steric hindrance; and (5) effect of neighboring groups. Based upon IR, NMR, and kinetic data, it was con-

cluded that in this study the $\begin{array}{c} \text{O} \\ \diagup \\ \text{C}=\text{N}^+ \\ | \end{array}$ structure did not greatly influence the rate of reaction of DHEU, DMeDHEU, and DMDHEU with cotton cellulose and that reaction with these compounds proceeded through their ring hydroxyls. With DHEU and DMeDHEU, where the same shift in C=O frequency was achieved even in the absence of the metal salt catalyst, it is possible that in acid media protonation of ring hydroxyls occurred. Such protonation (demonstrated below with DHEU) followed by loss of a

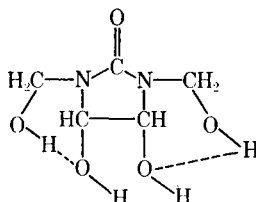


water molecule would result in formation of mesomeric ions which involve electrons of the ring carbon and nitrogen atom. Formation of such resonance structures should reduce mesomeric activity between electrons of the carbonyl group and nitrogen atom, thereby lessening the ability of the carbonyl groups of DHEU and DMeDHEU to coordinate protons (i.e.,

reducing contribution of $\begin{array}{c} \text{O} \\ \diagup \\ \text{C}=\text{N}^+ \\ | \end{array}$ structure) and increasing the double bond character of the carbon-oxygen bond, as evidence in the IR spectra of DHEU- and DMeDHEU-cellulose products. Formation of a carbonium ion as one of the resonating structures indicated that reaction with DHEU and DMeDHEU proceeded by an S_N1 mechanism, confirming a different mechanism from that of the DMEU-cellulose reaction and accounting for the observed large positive ΔS^\ddagger values. The fact that reaction of cotton

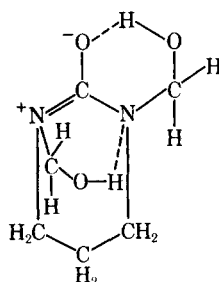
* The carbonyl wave numbers for EU and PU given by Petersen are 1704 and 1656 cm.⁻¹, respectively, and are not in agreement with values reported by others (Mecke-Hall, Berni, et al.).^{19,20}

cellulose proceeded much more rapidly with DMeDHEU than with DHEU could be attributed to the more electronegative environment of its ring hydroxyl, making protonation at these sites easier. Although DMDHEU, like DHEU and DMeDHEU, reacted with cotton through its ring hydroxyls, its rate of reaction was considerably slower than that of DMeDHEU but approximately equal that of DHEU. This was probably due to hydrogen bond formation between methylol and ring hydroxyls of the DMDHEU molecule, resulting in the indicated structure:



The methylol hydroxyl was the proton donor, and the labile hydrogen was attached to the ring hydroxyl as in DHEU. Such a structure would account for ΔH^* of activation with cotton being higher for DMDHEU than for DHEU since hydrogen bonds must be broken before reaction with cellulose occurs and would also account for the much more positive ΔS^* indicating greater disorder in the activated complex than in original reactants. Such a structure would also account for no additional shift in C=O band of IR spectra of DMDHEU-finished cottons.

DMPU, like DMEU, reacted with cellulose through its methylol hydroxyls and at the same rate, but reaction proceeded by a different mechanism. NMR proton signals for the two methylol groups on DMPU were not equivalent as were those of DMEU.¹⁸ Based on NMR data, it has been postulated that the DMPU molecule has two intra-H-bonds as shown:



Additionally, of compounds investigated, DMPU exhibited the weakest carbon-oxygen double bond character, and reaction with cellulose produced no further change in nature of this carbon-oxygen bond (based on IR) either in presence or absence of metal salt catalyst. However, in presence of catalyst, the N—C—N vibration was shifted to higher frequency. These shifts in presence of metal salt catalysts were similar to those observed by Berni²⁰ in the formation of PU-metal complexes where it was concluded that O → metal coordination occurred. Activation parameters indicate

that the DMPU-cellulose reaction was enthalpy controlled since ΔS^* was essentially zero. Although reaction with cellulose in absence of catalyst had no effect upon the carbonyl frequency, the C—N absorption was greatly reduced in intensity, appearing only as a shoulder. In addition, no improvement in crease recovery of the cotton fabric was achieved in uncatalyzed reaction products. Therefore, it is hypothesized that in absence of catalyst, cellulose reaction took place only at that methylol hydroxyl of DMPU which is H-bonded to the nitrogen atom and did so without disturbing the remainder of the DMPU network. In catalyzed reactions, $O \rightarrow Zn^{++}$ coordination occurs, thereby freeing the methylol group originally H-bonded to the carbonyl for reaction with cellulose. Such mode of reaction would account for a rate similar to that of DMEU when both methylol hydroxyls are equivalent. Earlier investigations,⁶ which further lend support to this theory, have shown that the total amount of Zn^{++} furnished by the catalyst was retained by DMPU-finished cottons and that enhanced crease recovery was obtained only when a Lewis acid catalyzed the reaction.

Summary

The structure of the cyclic urea influenced the rate of reaction with cotton cellulose and the mechanism by which reaction occurred. Although rates of reaction of cotton cellulose were the same for $Zn(NO_3)_2$ catalyzed DMEU and DMPU reactions, activation parameters indicated different modes of reaction. DMEU reaction was entropy controlled, while DMPU was enthalpy controlled. Large negative ΔS^* values for DMEU indicated a more ordered transition state complex and an S_N2 mechanism while the essentially zero ΔS^* obtained for DMPU indicated that there was no difference in order of activated complex and original reactants. Reaction of DMEU and DMPU with cellulose proceeded through methylol hydroxyls; and although IR and NMR spectra indicated differences in electron density on the ring nitrogens of these two reagents, the rates of reaction were equal. With DMEU-cellulose reactions, $N \rightarrow$ metal coordination resulted when metal salt catalysts were employed. With DMPU-cellulose reactions, $O \rightarrow$ metal coordination occurred with catalysts. NMR proton signals were not equivalent for the methylol groups of DMPU. In reaction of cellulose with DMPU in the absence of catalyst, it is hypothesized that reaction occurs at the methylol hydroxyl originally bonded to the ring nitrogen. In presence of catalyst, $O \rightarrow$ metal coordination frees the methylol hydroxyl bonded to the carbonyl group, and reaction with cellulose takes place through both methylol hydroxyls as with DMEU where both methylol hydroxyls are equivalent.

The IR, NMR, and kinetic data indicated that mesomeric activity between electrons of carbonyl oxygen and nitrogen atom had little influence on the rate of reaction of DHEU, DMeDHEU, and DMDHEU with cotton cellulose and that reaction of these compounds proceeded through their ring hydroxyls. Protonation of ring hydroxyls of DHEU and DMeDHEU

followed by loss of a water molecule has been hypothesized as the mechanism by which reaction with cellulose takes place. Such protonation results in resonance structures involving a carbonium ion and, thus, indicated an S_N1 mechanism for these reactions. The much faster rate of reaction of DMeDHEU-cellulose reactions has been attributed to the more electronegative environment of its ring hydroxyl, making it more readily protonated. Hydrogen bonding between methylol and ring hydroxyls of the DMDHEU molecule, in which the methylol hydroxyl is the proton donor, has been proposed to account for observed changes in character of IR absorption spectra and slower rate of reaction of cellulose with DMDHEU than with DHEU or DMeDHEU.

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