

The Reaction of Activated Vinyl Compounds with Cotton Cellulose via Internal Catalysis

STANLEY P. ROWLAND and MARY ANN F. BRANNAN,
*Southern Regional Research Laboratory, Southern Utilization
Research and Development Division, Agricultural Research Service,
U. S. Department of Agriculture, New Orleans, Louisiana 70119*

Synopsis

The reactions of a variety of activated vinyl compounds with cotton cellulose fabric containing quaternary ammonium hydroxide substituents were explored. Each reaction, catalyzed by the basic groups in the cellulose, was followed to or near the point of leveling off. The results are analyzed and discussed in terms of accessibility of the cellulosic compositions and in terms of the efficiency of the quaternary ammonium substituents as catalysts for the addition reactions. Estimates of relative forward rate constants (k_f) and equilibrium constants (K) for the reactions were made. The values of k_f for reactions of the vinyl compounds with the quaternary ammonium celluloses show a relative order which is similar to that for the reactions of the vinyl compounds with simple alcohols. Evidence is presented to indicate that, in some cases, the addition of vinyl compounds is accompanied by anionic-catalyzed graft polymerization.

INTRODUCTION

The addition of cellulosic hydroxyl groups to reagents containing activated double bonds is of considerable interest in the chemical modification and crosslinking of cellulose.¹⁻⁴ Catalysis of reactions of cellulose by special groups that are built into the cellulosic structure offers possibilities for conducting reactions without the necessity for conventional (external) catalysts and for achieving reactions and results which are not possible via conventional catalysis.^{5,6}

In connection with the investigation of thermally reversible crosslinking reactions in cotton cellulose, the reactions of cellulosic hydroxyl groups with activated vinyl compound have taken on a new interest, particularly in cellulosic compositions in which basic catalyst groups are built into the polymeric structure for in situ catalysis.⁶⁻⁸

This paper reports the results of an exploration of reactions of cotton cellulose containing quaternary ammonium base substituents with a variety of activated vinyl compounds. Relative kinetic and equilibrium data are reported and compared to published results from conventional reactions with external catalysts.

EXPERIMENTAL

Materials

The following reagents were used without further purification: divinyl sulfone, ethyl vinyl sulfone, methyl vinyl ketone, and ethyl vinyl ketone (Monomer-Polymer Laboratories, Borden Chemical Company); acrylonitrile (practical) and fumaronitrile (Baker grade) (J. T. Baker Chemical Company); methyl vinyl sulfone (K & K Laboratories); methacrylonitrile (Shell Development Company); acrylamide and *N,N'*-methylenebisacrylamide (Eastman Organic Chemicals); maleimide (Aldrich Chemical Company).

Quaternary ammonium cotton fabrics used in this study, designated Quat I and Quat II, were prepared and characterized as described previously.^{6,7} Quat I designates that fabric resulting from padding treatment of 80 × 80 cotton print cloth with a 20% aqueous solution of 2-chloroethyl-diethylamine hydrochloride (diethylaminoethyl chloride hydrochloride) followed by immersion in hot 8% NaOH⁹ and subsequent quaternization of this diethylaminoethyl cellulose fabric with methyl iodide.^{10,11} Nitrogen content of Quat I fabric used in this study was 0.45%. Quat II designates that fabric prepared from the reaction of 3-chloro-2-hydroxypropyltrimethylammonium chloride with 80 × 80 cotton print cloth in the presence of 20% NaOH.⁷ Nitrogen content of Quat II used for this study was 0.45%.

Reactions of Activated Vinyl Compounds With Quaternary Ammonium Cotton Fabrics

Samples of the respective quaternary ammonium cotton fabrics, 2 × 3 in., weighing 0.4–0.5 g each, were put into the base form by soaking 15 min in 50 ml of 0.05*N* NaOH. The fabrics were rinsed in deionized water until free of NaOH; while still retaining approximately 100% wet pickup of the deionized water, each sample of fabric was immersed in a measured quantity of reagent solution preheated to 30.2°–30.4°C. (Fabrics to be reacted with dilute ethyl vinyl ketone were subsequently padded through dimethyl sulfoxide (DMSO) prior to addition to the reaction solution because of the insolubility of the vinyl compound in the presence of water.) The reagent solution was four times the weight of the dry quaternary ammonium hydroxide fabric. Original concentrations of vinyl compounds in the reagent solutions were 12.5% and neat. (Since acrylamide is a solid, it was applied to the damp fabric as a 53% solution in water.) The dilute solutions contained 12.5% by weight of each of the activated vinyl compounds dissolved in water, DMSO, water–DMSO combinations, or dimethyl formamide, depending on solubilities of the individual compounds. On addition of the wet quaternary ammonium hydroxide cotton fabrics to the reagent solutions, the effective concentrations of reagent dropped to approximately 10.0% (or to 80% from neat) and the weight ratio of solution to fabric was 5:1. This is little more solution than required to wet

the fabric. Reactions were continued for 16 hr at 30.2°–30.4°C; at the appropriate time intervals, reactions were halted by rinsing the fabric samples in tap water. The fabrics were then soaked 5 min in 1% acetic acid, rinsed in distilled water, and air-equilibrated 16–24 hr prior to determination of the extent of incorporation of reagent by weight gain, elemental analysis, or infrared spectroscopic analysis.

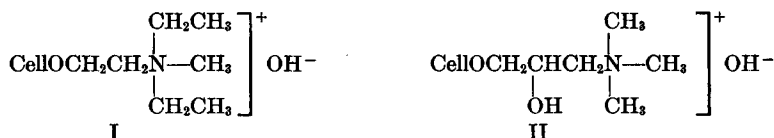
Analysis

Sulfur and nitrogen analyses of the fabrics were determined by conventional microanalytical and micro-Kjeldahl methods, respectively. Crystallinity indices were based on x-ray diffractograms obtained with a General Electric automatic recording diffractometer equipped with copper target, nickel filter, and medium-resolution Soller slits, using standard techniques.¹² The type of crystalline lattice and the extent of order in the cellulosic compositions were determined by the method of Patil et al.¹³ Infrared spectra were obtained from KBr discs using a Perkin Elmer 21 spectrophotometer equipped with NaCl optics.

RESULTS AND DISCUSSION

The Cellulosic Substrates for the Reactions

Two chemically modified cotton celluloses in the form of print cloth served as substrates for the internally catalyzed reactions which are described in the following sections. The quaternary ammonium cotton cellulose (designated Quat I) which is the basis for the major portion of the study was prepared by introduction of 2-(diethylamino)ethyl substituents into the cellulose followed by quaternization and conversion to the base form. The nature of these substituents is shown in structure I.



The crystalline lattice structure of the native cotton cellulose was not altered by these chemical treatments, i.e., the crystallinity indices¹² of the original cellulose and the Quat I were 88 and 90, respectively.

A second quaternary ammonium cellulose (Quat II) was prepared directly in the base form from the reaction of 3-chloro-2-hydroxypropyltrimethylammonium chloride with cellulose. The nature of the substituents is shown in structure II above. The lattice structure of the cellulose underwent substantial change in this case, the lattice I being reduced from 88% to approximately 35% with substantial development of lattice II structure from the mercerizing caustic employed in the preparation of Quat II.¹³

The quaternary ammonium celluloses contained the same amount of nitrogen (0.45%), an indication that the extent of substitution of qua-

ternary ammonium substituents is the same in both cases (i.e., 0.0322 moles of substituent per 100 g of quaternary ammonium cotton cellulose, or a degree of substitution of 0.055).

It is estimated that the radius of motion of the water-solvated and extended 2-(diethylmethylammonium)ethyl substituent of Quat I (or the corresponding substituent of Quat II) attached to the surface of the crystalline microstructural unit in cotton cellulose may allow the quaternary ammonium group to come in close proximity to approximately ten hydroxyl groups on the same surfaces. Dreding molecular models and the dimensions of the unit cell of cellulose were employed in this estimation. The sphere of influence of the hydroxyl ion that attends the quaternary ammonium unit is expected to be larger; thus, the catalytic action of the quaternary ammonium group in ionizing cellulosic hydroxyl groups might be effective over an area of surface containing 20 or more hydroxyl groups.

It is assumed that the accessibility of the hydroxyl groups of Quat I is comparable to that of the original cotton cellulose,^{14,15} i.e., in the range of 10% to 20% (0.30 to 0.60 hydroxyl groups per glucopyranosyl unit). Then the quaternary groups in Quat I, that are present at a degree of substitution of ca. 0.06, may be associated with accessible hydroxyl groups in ratios from 0.06 : (0.30-0.06) to 0.06 : (0.60-0.06), or 1:4 to 1:9.

In Quat II, there is a substantially higher accessibility of hydroxyl groups due to the mercerization of the cellulose.¹⁵ At assumed accessibilities of 20% to 35%, the ratio of quaternary groups in Quat II to accessible cellulosic hydroxyl groups is 1:9 to 1:17.

From these considerations it appears likely that all of the accessible hydroxyl groups in these samples of Quat I and Quat II are within the sphere of catalytic activity of the quaternary substituents groups.

Reactions of Activated Vinyl Compounds in Dilute Solutions With the Internally Catalyzed Celluloses

The Overall Reactions. Each activated vinyl compound, at 10% concentration in solution, was allowed to react with Quat I and Quat II fabrics for various periods of time at 30.2°-30.4°C. To facilitate comparisons, the results are expressed as the number of moles of reagent residues incorporated into 100 g of the quaternary ammonium cellulose.

The progressions of the additions of the lower-reactivity vinyl compounds to Quat I fabric are shown in Figure 1 and those of the higher-reactivity vinyl compounds are plotted in Figure 2. The courses of these reversible reactions are generally similar, i.e., the amount of the vinyl compound added to the cellulosic hydroxyl groups increases with duration of the reaction to reach a maximum. A stable maximum indicates that equilibrium has been reached, whereas a subsequent decrease is consistent with consumption of vinyl compound through a side reaction with water.^{16,17}

The crystallinity of the cellulose showed very little change as a result of these 16-hr reactions. Crystallinity indices remained above 86 for most of the products; the products from reactions involving vinyl sulfones con-

TABLE I
Parameters for Reactions of Activated Vinyl Compounds with Quaternary Ammonium Celluloses

Vinyl compound	Reagent solvent (water DMSO ratio) ^a	Max. moles of bound reagent/100 g of Quat ^b		Max. moles of bound reagent/quaternary group ^c		Max. moles of bound reagent/equiv. of cellulosic hydroxyl	
		Quat I	Quat II	Quat I	Quat II	Quat I	Quat II
N,N'-Methylene-bisacrylamide	20:70 ^d	0.0083	—	0.26(0.52)	—	0.005	—
Maleimide	70:20	0.0122	—	0.38	—	0.007	—
N-Methylolacrylamide	90:—	0.0138	—	0.43	—	—	—
Acrylamide	90:	0.0321	0.0412	0.99	1.3	0.018	0.023
Methacrylonitrile	33:57	0.0347	—	1.1	—	0.019	—
Ethyl vinyl ketone	—:90	0.0820	—	2.6	—	0.046	—
Fumaronitrile	26:64	0.0829	0.1135	2.6	3.5	0.045	0.064
Divinyl sulfone	80:10	0.1141	0.3041	3.6	9.5	0.064	0.171
Methyl vinyl sulfone	90:—	0.1271	0.2714	4.0(8.0)	8.4	0.072	0.153
Ethyl vinyl sulfone	90:—	0.1604	—	5.0	—	0.090	—
Acrylonitrile	52:38	0.2596	0.5510	8.1	17.2	0.134	0.309
Methyl vinyl ketone	36:54	0.5070	0.3183	15.8	9.9	0.285	0.379

^a The reagent (10%) in contact with the cellulose was dissolved in water:DMSO in the percentages indicated.

^b At the maximum level of incorporation of reagent residues into the cellulose.

^c Maximum moles of reagent incorporated into the cellulose per quaternary substituent. Values in parenthesis are equivalents of vinyl units per quaternary substituent.

^d Dimethyl formamide was required in this case in place of DMSO.

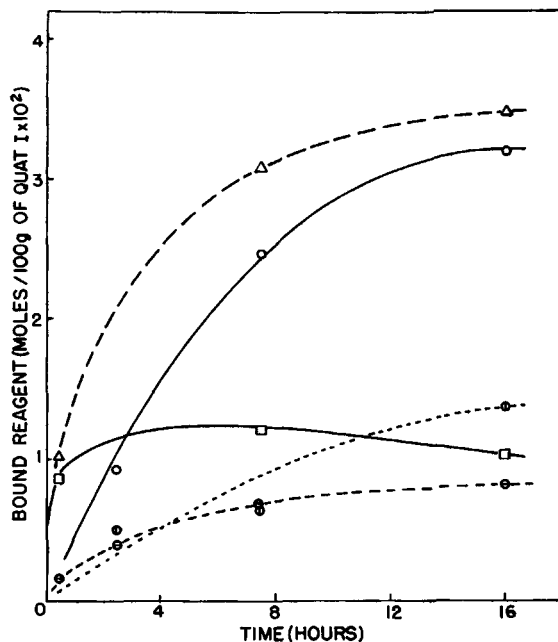


Fig. 1. Reactions of "low-reactivity" activated vinyl compounds with Quat I fabric: (Δ) methacrylonitrile; (O) acrylamide; (\square) maleimide; (\oplus) *N*-methylolacrylamide; (\ominus) *N,N'*-methylenebisacrylamide.

stituted the exceptions and exhibited crystallinity indices of 78–82. It may be concluded that at most the changes in crystallinity were small and that, in the majority of cases, the final crystallinity indices are in the same range as that of the original cellulose (i.e., 88).

Qualitatively, the reactions of the vinyl compounds with Quat II fabric (see Fig. 3) are quite similar to those with Quat I fabric. With one exception (methyl vinyl ketone), however, the reactions of Quat II proceeded to incorporate a higher level of each vinyl compound into the cellulose. The higher level of reaction of activated vinyl compounds with Quat II is most readily apparent from data summarized in Table I (columns 3, 4, 7, and 8). Generally (excepting methyl vinyl ketone), approximately 30% to 170% more reagent was incorporated into Quat II fabric than into Quat I fabric. The major portion of these differences is attributed to differences in accessibility (see preceding section), but a portion of the difference could be due to the reactive hydroxyl group present in the substituent group in Quat II. This hydroxyl group could raise the moles of bound reagent, at maximum, by 0.0322 per 100 g of quaternary ammonium cotton cellulose.

Additional insight into these reactions is obtained by considering the maximum moles of bound reagent per equivalent of cellulosic hydroxyl group. Only two of the reactions with Quat I proceed to the extent that they involve the major portion of the accessible hydroxyl groups, i.e.,

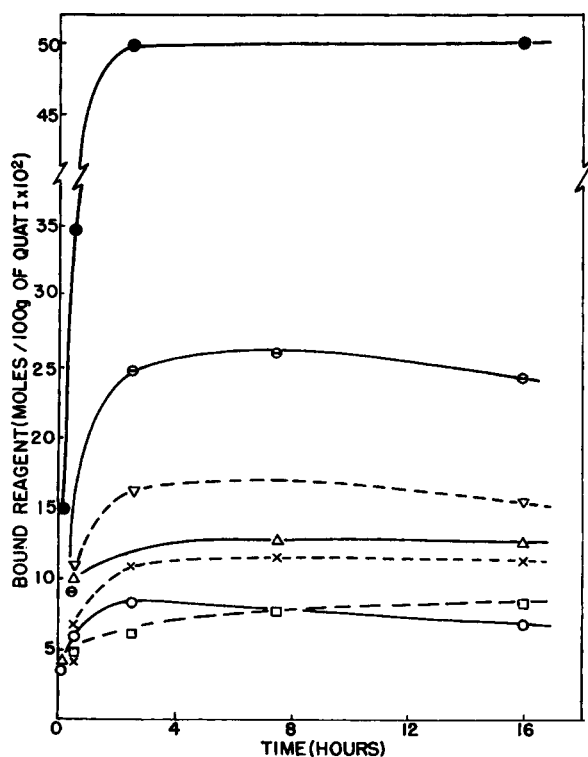


Fig. 2. Reactions of "high-reactivity" activated vinyl compounds with Quat I fabric: (●) methyl vinyl ketone; (⊖) acrylonitrile; (∇) ethyl vinyl sulfone; (Δ) methyl vinyl sulfone; (×) divinyl sulfone; (□) fumaronitrile; (○) ethyl vinyl ketone.

acrylonitrile apparently involves 13.4% of the total hydroxyl groups and methyl vinyl ketone apparently involves 28.5% (Table I, column 7). Since the limit of accessibility has been estimated to be in the range of 10%–20% of the total hydroxyl groups, and since decrystallization did not occur, there is reason to suspect that some of these reagent molecules may have formed graft chains in the cellulose. While the formation of graft chains may occur in Quat II, the data (Table I, column 8) do not provide as pronounced an indication.

Efficiencies of the Quaternary Groups. At the maximum level of reaction of each vinyl compound with Quat I or Quat II fabric, the number of moles of reacted vinyl compound per quaternary ammonium substituent varies considerably (Table I, columns 5 and 6). On the average, a single quaternary substituent of Quat I catalyzed reactions of 0.3 to 16 vinyl units. For a given vinyl compound, the quaternary ammonium group in Quat II is generally more effective in terms of the amount of vinyl compound reacted per quaternary group.

The highest level of reaction with Quat I fabric introduces more units of vinyl compound per quaternary substituent (i.e., 15.8) than the number of

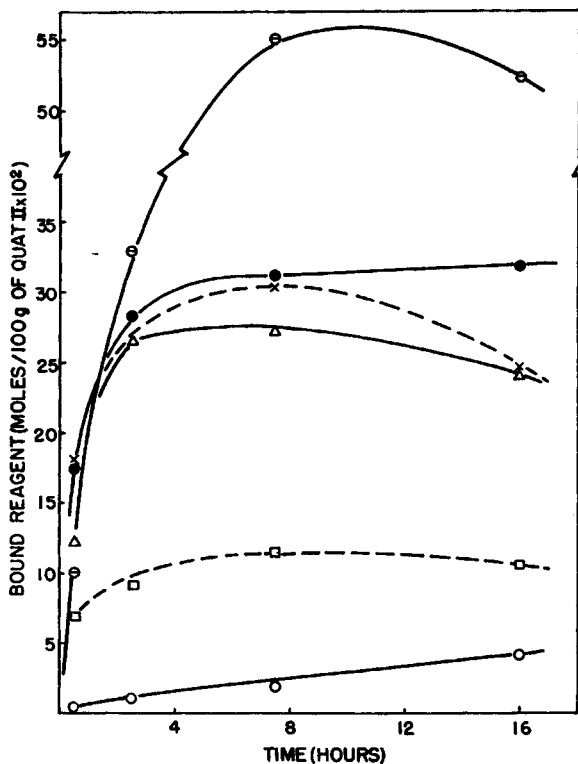


Fig. 3. Reactions of activated vinyl compounds with Quat II fabric: (●) methyl vinyl ketone; (⊖) acrylonitrile; (Δ) methyl vinyl sulfone; (×) divinyl sulfone; (□) fumaronitrile; (○) acrylamide.

accessible hydroxyl groups that is estimated to be available (i.e., 9; see preceding section). In the case of Quat II, the highest level of reaction falls within the estimated range of accessible hydroxyl groups. However, the inference is that in the case of reactions with methyl vinyl ketone and acrylonitrile some grafting may occur as well as the addition of single units of the vinyl compound to the cellulosic hydroxyl groups.

Kinetics and Equilibria of the Reactions. The substantial differences in the shapes and heights of the curves in Figures 1 to 3 suggest that there are pronounced differences in the kinetics and equilibria of the reactions of the various vinyl compounds. For the purpose of gross comparisons among the reagents, values have been estimated for the forward rate constants (k_f) and for the equilibrium constants (K) for the reactions. Since these reactions take place within the fibrous structure of cotton cellulose with that fraction of hydroxyl groups which is accessible and which is reached by diffusion of the reagent, rigorous kinetic analysis requires knowledge of the activities of the hydroxyl groups in the solid cellulose and of the absolute accessibilities of the hydroxyl groups. Values of k_f and K which are suitable for limited comparative purposes may be obtained by

introduction of two assumptions and simplifications: (1) by the expression of the "concentrations" of the hydroxyl groups of the cellulose in terms of moles per liter (although the expression is arbitrary, it is pertinent that all of the experiments were conducted at same "concentration" of cellulose); and (2) by the assumption that the same fraction of hydroxyl groups is accessible to each of the vinyl compounds; while this is considered generally reasonable in these cases, similar-to-identical accessibilities are most likely for the vinyl compounds which are reacted from aqueous or partially aqueous systems; arbitrarily, the value of accessibility is taken as 20% for both Quat I and Quat II fabrics (see preceding section).

The reactions of activated vinyl compounds with the quaternary ammonium celluloses are treated as reversible reactions,¹⁶ as expressed below (R designates the reagent):



Side reactions¹⁶ are neglected. The kinetic treatment employs eqs. 2 to 4 and the fitting of these equations to curves of [CellOR] plotted versus duration of reaction:

$$\frac{d[\text{CellOR}]}{dt} = k_f[\text{CellOH}][\text{R}] - \frac{k_f}{K}[\text{CellOR}] \quad (2)$$

$$[\text{R}] = [\text{R}_0] - [\text{CellOR}] \quad (3)$$

$$[\text{CellOH}] = [\text{CellOH}_0] - [\text{CellOR}] \quad (4)$$

Terms in brackets indicate concentrations in moles per liter of the specific reactive group. Subscript zero designates the initial concentration. The fitting of curves was carried out with an analog computer.

The values of k_f and K for reactions of Quat I and Quat II fabrics are summarized in Table II. It may be noted that the relative order of values of k_f for reactions involving Quat I fabric (column 4, Table II) is quite similar to that for the homogeneous reactions of these reagents with simple alcohols as reported by Ring et al.¹⁸ (column 6, Table II). Thus, the values of k_f decrease in each of these series for reactions in the following order: methyl vinyl ketone, divinyl sulfone, fumaronitrile, acrylonitrile, and acrylamide. Deviations of approximately one position in the order of k_f values in the two series occur for ethyl vinyl ketone, methacrylonitrile, and N,N'-methylenebisacrylamide. Ethyl vinyl sulfone (and methyl vinyl sulfone) shows greater deviation, being lower in k_f than divinyl sulfone in homogeneous reactions with methanol but higher in k_f in heterogeneous reaction with cellulose.

The results with Quat II fabric, while quite limited in scope, indicate substantial variation in order of k_f values from that of Quat I fabric. This may be a reflection of the unpredictable and large variation in accessibility of a mercerized cotton from one reagent to another.

TABLE II
Estimated Equilibrium (K) and Forward Rate Constants (k_f) for Reactions of Activated Vinyl Compounds with Cellulose at 30.2°–30.4°C^a

Compound	K		k_f , l./mole-min		
	Quat I	Quat II	Quat I	Quat II	Literature ^b
N,N'-Methylenebisacrylamide	0.040	—	0.00018	—	0.0165 ^c
Maleimide	0.038	—	0.0020	—	—
Acrylamide	0.091	0.124	0.00018	0.00022	0.0294 ^c ; 0.019 ^d
Methacrylonitrile	0.072	—	0.0007	—	0.0115 ^d
Ethyl vinyl ketone	0.307	—	0.0146	—	14.1 ^e
Fumaronitrile	0.274	0.486	0.010	0.0083	5.96 ^e
Divinyl sulfone	0.800	27.8	0.0185	0.046	11.38 ^e
Methyl vinyl sulfone	0.849	8.86	0.033	0.030	—
Ethyl vinyl sulfone	1.63	—	0.023	—	2.46 ^e
Acrylonitrile	1.95	<i>f</i>	0.0076	<i>f</i>	0.732 ^e
Methyl vinyl ketone	<i>f</i>	12.1	0.035 <i>f</i>	0.014	26.4 ^e

^a Based on estimated accessibilities of 20% for both Quat I and Quat II.

^b For homogeneous reactions with methanol or 2-propanol at 24°C.¹⁸

^c 50% 2-propanol in dimethylformamide with 0.3*N* potassium 2-propoxide.

^d 2-Propanol with 0.3*N* potassium 2-propoxide.

^e Methanol with 0.03*N* sodium methoxide.

^f These reactions proceeded to introduce molar quantities of reagent residues equivalent to 30.9 and 28.5% of the total hydroxyl groups for the acrylonitrile and methyl vinyl ketone, respectively.

It is interesting to note for order of magnitude that in many cases the estimated values of k_f for reactions involving Quat I or Quat II fabrics are 0.01 to 0.002 times the values for the corresponding reactions involving the simple alcohols. A difference of this magnitude is quite reasonable since the k_f values for the reactions of the quaternary ammonium cotton celluloses involve the composite of diffusion and chemical reaction.

Although the values estimated for K are very sensitive to the value of the accessibility assumed for the kinetic analysis, the K 's listed in Table II provide useful relative values for those reactions of Quat I or Quat II for which the accessibilities are similar. Therefore, comparisons of K 's should be limited to the reactions of a specific cellulosic composition. Furthermore, it is suspected that the low K and k_f for ethyl vinyl ketone (these values were expected to be second only to those for methyl vinyl ketone¹⁸) are due to the low accessibility of hydroxyl groups to this reagent, which required a completely nonaqueous system. It is suspected that the differences in K 's for a given vinyl compound reacting with Quat I or Quat II fabric (and the differences in orders of k_f values for reactions of Quat I, Quat II and simple alcohols) are due to subtle differences in accessibilities of the hydroxyl groups to the various reagents.

In a rather general way, the results noted above bear out the prediction of Tesoro³ that the relative order of reactivity established in suitable model experiments (i.e., with simple alcohols¹⁸) is generally maintained for reac-

tions of cellulosic fibers; however, the results also emphasize that the order of reactivity can change very substantially from simple alcohols to cotton cellulose and that this is very probably due to differences in accessibilities of the reagents.

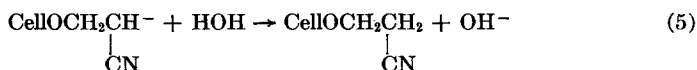
It is likely that the rather good agreement between relative orders of reactivity of vinyl compounds with Quat I fabric and with simple alcohols is due, in part, to the low degree of side reactions in each of these cases. Side reactions in the conventional, externally catalyzed reactions of activated vinyl compounds with cellulose may account for the deviations from these orders.¹

Reactions of Activated Vinyl Compounds in High Concentrations With the Internally Catalyzed Celluloses

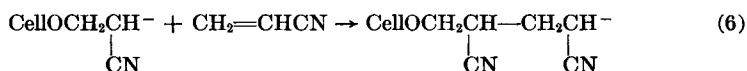
The effect of contacting the moist quaternary ammonium cellulose fabric with the neat activated vinyl compound varied with the compound. For example, (a) the vinyl sulfones and ethyl vinyl ketone reacted to significantly lesser extents than in the dilute media, (b) methacrylonitrile reacted to the same extent as from the dilute medium, (c) methyl acrylate reacted to a measurable extent (i.e., 0.016 moles/100 g of Quat I in 16 hr) and acrylamide reacted approximately 35% more than in the dilute medium, and (d) acrylonitrile and methyl vinyl ketone showed increases in the extent of reaction amounting to approximately 200% (i.e., to 0.36 and 0.86 moles of reagent, respectively, per equivalent of hydroxyl group of Quat I in 16 hr).

The extents of reactions of acrylonitrile and methyl vinyl ketone, which are noted above, are based on samples that had been subjected to extraction with dimethylsulfoxide; none of the acrylonitrile residues and only 24% of the methyl vinyl ketone residues were extractable. In some cases, the swelling of the acrylonitrile residues during extraction was sufficient to disrupt the fabric and fiber structures, leaving a structureless gel.

Since crystallinity indices of the cellulosic compositions decreased very little as a result of these reactions, it appears that reaction was limited to the normally accessible hydroxyl groups; and it is concluded that substantial graft polymerization occurred during the reactions of acrylonitrile and methyl vinyl ketone. These monomers are highly susceptible to polymerization by anionic catalysis. Whether the initial addition of the acrylonitrile to the cellulosate ion is followed by the abstraction of a proton from water, as in eq. (5), or is followed by the addition of another unit of



acrylonitrile, as in eq. (6), depends upon the concentrations of water and



acrylonitrile and the rate constants for the two reactions.

This controllable transition from cyanoethylation to graft polymerization of cotton cellulose appears to be unique to this system; in conventional reactions of fibrous cellulose employing external catalysis, cyanoethylation and controlled graft polymerization appear to be mutually exclusive.^{19,20}

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