

Reaction of Formaldehyde with Cellulose Xanthate

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Synopsis

Formaldehyde reacts reversibly with cellulose xanthate in aqueous acid to form a product having an absorption maximum at 280 $m\mu$ and an extinction coefficient of 11,600. The fraction of the original xanthate converted to the formaldehyde form is related to the formaldehyde concentration. The aqueous acid decomposition rate of the formaldehyde derivative is pseudo first-order and is inversely proportional to the formaldehyde concentration. At high acidities the decomposition rate is independent of acid concentration, but the rate decreases with decreasing acidity in the pH range of 1-4. On the basis of the data obtained in these studies, the equilibrium constant for the formation of the formaldehyde derivative was found to be of the order of $10^{4.8}$. The activation energy for the decomposition of the formaldehyde derivative is 18,600 cal./mole.

INTRODUCTION

During the course of the many years that viscose has been manufactured, it has been quite a challenge to find as many chemicals as possible which could be added to the process in order to change the properties of the final product. Of the many compounds studied, formaldehyde is one of the few which have been found to react with the cellulose xanthate. It appears that Alles¹ is the first investigator to have recognized that this material forms a derivative. Alles gives no quantitative data, but his qualitative statements for the most part are confirmed by the present work. A number of other patents have been issued on the use of formaldehyde.²⁻⁶ They, generally, do not mention the formation of a definite chemical compound.

All of the patentees, in general, used formaldehyde in concentrations of the order of 0.1-5.0% in the spinning bath or cascade in order to permit a higher stretch of the yarn. The addition of the formaldehyde to the viscose has also been considered.⁴

The ultraviolet film technique⁷ presented a convenient means of studying the reaction of formaldehyde with cellulose xanthate. In this work the cellulose xanthate was exposed to various solutions containing formaldehyde, including ordinary rayon spin baths.

The results reported below presuppose that a competitive reaction occurs when acid and formaldehyde are added to cellulose xanthate. Other studies⁷ have shown that an acid or acids form from cellulose xanthate.

EXPERIMENTAL

Materials

Baker and Adamson reagent grade formaldehyde solution containing 36–38% formaldehyde and 10–15% methanol preservative was used for the experiment. All other chemicals were reagent grade.

In order to eliminate unknown variables from differences in age and composition, a viscose having the composition of 7.5% cellulose, 6.5% NaOH, and 40% CS₂ was prepared from additive-free pulp and aged for three days. All the viscoses were ion-exchanged to eliminate competing reactions which might occur with the by-products.

Equipment

The equipment and general methods have been described previously.⁷ In this work a Cary Model 14 spectrophotometer, as well as a Beckman DK-1, was used.

The cell holder was maintained at the desired temperature by means of the constant temperature bath. Spinning bath containing the desired amount of the aldehyde was placed in the reference cell and the absorbance was adjusted to zero at 303 m μ with a dry cell containing the optical flat in the sample beam. A thin film of ion-exchanged viscose was next cast on the optical flat of the sample cell and the absorbance measured at 303 m μ . This value should be between 1.0 and 2.0. The wavelengths of 280 m μ was then set and the ratio of the absorbance at 280 m μ to that at 303 m μ determined. If this ratio exceeded 0.18, it indicated that some imperfection or impurities existed in the viscose film which would likely lead to high background after reaction and the film was therefore discarded. Spinning bath solution containing the formaldehyde was injected in a smooth even motion into the sample cell containing the optical flat with the viscose film. The recorder was allowed to run during the injection operation and for a sufficient time interval afterward. Preliminary experiments indicated that, with a properly prepared film, the background at 280 m μ after complete acid decomposition of the film was essentially zero.

RESULTS

Qualitative Studies of the Requirements for the Reaction

When an aqueous formaldehyde solution is in contact with sodium cellulose xanthate, there is no evidence (no change in ultraviolet spectrum) of any reaction until acid is added. When strong acid is also present, there is a drastic shift in the absorption maximum to 280 m μ with no indication of any other species being present. This effect is shown in Figure 1.

The aldehyde derivative is relatively stable to acid and elevated temperatures, provided an appreciable excess of formaldehyde is present. It is rapidly converted back to the xanthate ion form on addition of sodium hydroxide. Removal of the formaldehyde solution from the cell and sub-

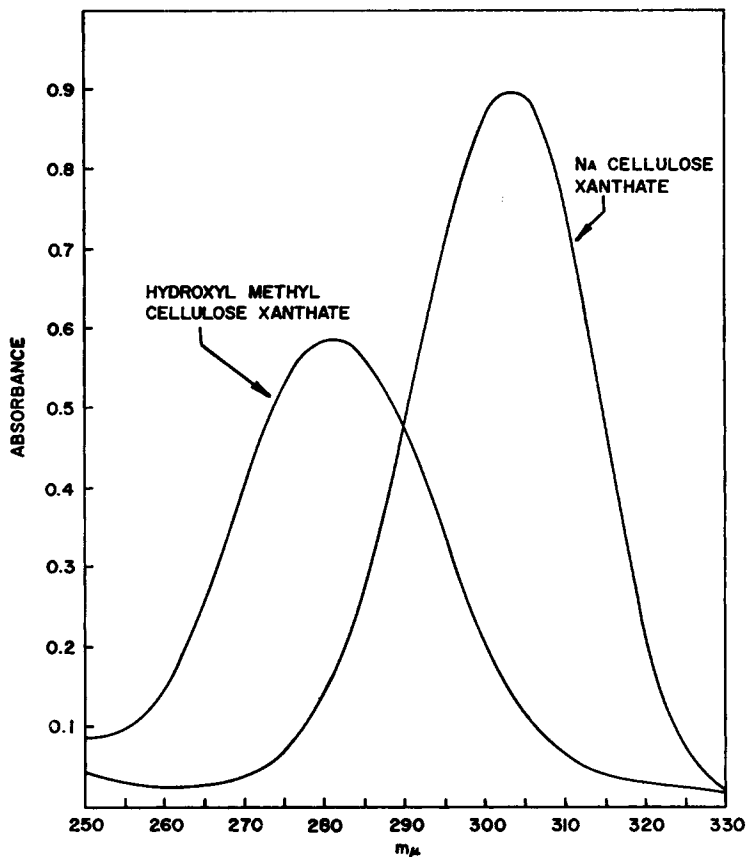
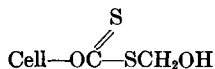


Fig. 1. Ultraviolet spectra of sodium cellulose xanthate and *S*-hydroxymethyl cellulose xanthate. Essentially complete formation of the derivative is indicated by the absence of a shoulder at 303 $m\mu$.

stitution of distilled water, sodium bisulfite, or acid solutions results in a rapid loss of all absorbance (decomposition of the xanthate).

From the above observations, it may be concluded that formaldehyde reacts reversibly with the xanthate ion. It is not an oxidation product (such as dixanthate) since it can be quantitatively converted back to the xanthate ion in an alkaline system. One possible structure which has been proposed is



A model compound, the formaldehyde derivative of ethyl xanthate, was prepared by Thumm and Tryon,⁸ and various studies indicated a structure of this type.

The ultraviolet spectrum of the formaldehyde derivative is almost identical with that of *S*-methyl cellulose xanthate.⁷ Since the absorption

in the ultraviolet region may be traced to the double bond C=S structure, the effect of CH₃ or CH₂OH groups should be similar, and this supports the proposed structure.

Extinction Coefficients

The extinction coefficients of the *S*-hydroxymethyl cellulose xanthate can be determined by use of eq. (1):

$$A_x^{303}/A = \epsilon_x^{303} cl/\epsilon cl \quad (1)$$

where A_x^{303} is the measured absorbance at 303 m μ of the film of ion exchanged viscose (sodium cellulose xanthate), ϵ_x^{303} has a value of 15,900,⁹ A is the measured absorbance of the new species at the desired wavelength, and ϵ is the new extinction coefficient. The requirement which must be met for this to be used is that the product, cl , of the concentration and length of the light path of the absorbing species remain constant. This condition is met if quantitative conversion takes place with subsequent negligible decomposition within the measuring time interval.

This condition is approached when faintly acidic (pH > 2.0), very strong formaldehyde (about 5%) solutions are in contact with the viscose film at low temperatures. An alternate method is to form the formaldehyde derivative and, after measuring the absorbance at 280 m μ , reconvert the derivative to xanthate ion by replacing the formaldehyde solution with sodium hydroxide solution. The former method may possibly be preferable because of the time required to withdraw a solution from the cell and replace it, and also because of the possibility of dissolving the film in the caustic. The average of 24 results obtained by both methods is $\epsilon_d^{280} = 11,600$, with a standard deviation of 600.

The extinction coefficients of the other xanthate derivatives have been found to be in the range of 10,000–12,000.^{7,10} The agreement lends credence to the proposed structure for the formaldehyde derivative.

In order to calculate the concentrations of xanthate and the formaldehyde derivative which under certain conditions are found to be present simultaneously, values of the extinction coefficients at 280 m μ for the xanthate ion and at 303 m μ for the formaldehyde derivative are necessary. These were determined in the case of the xanthate ion by experimentally determining the ratio of the absorbances at 280 and 303 m μ on a number of sodium cellulose xanthate films. The value of the extinction coefficient can be calculated from: $A^{280}/A^{303} \times 15,900$. Since at 280 m μ the xanthate ion absorption curve has a very steep slope, a relatively large standard deviation was obtained. This is not as important as might be expected since the value of ϵ of the xanthate species at 280 m μ is only about 20% of that of the formaldehyde derivative. The extinction coefficient of the *S*-hydroxymethyl cellulose xanthate at 303 m μ was determined in the same manner. Again the measurement is on a steep slope but the value is only about 14% of that of the xanthate ion at the same wavelength and again would contribute only a small relative error for a large absolute

error. The data obtained from ten measurements each for these two extinction coefficients are: $\epsilon_d^{303} = 2180$, $\sigma = 280$, and $\epsilon_x^{280} = 2490$, $\sigma = 230$.

Experimental Rate Constant for the Acid Decomposition of *S*-Hydroxymethyl Cellulose Xanthate

The experimental data as taken are a plot of absorbance A versus time t at 280 $m\mu$. The absorbance increases rapidly immediately after addition of the acid formaldehyde solution, then decreases relatively rapidly for a

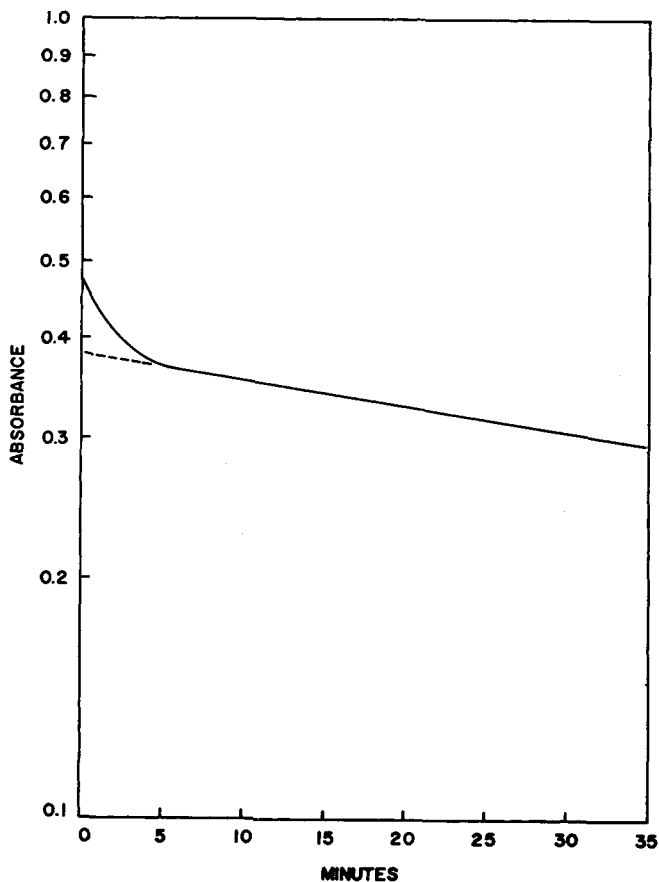


Fig. 2. Plot of the logarithm of the absorbance change which occurs when sodium cellulose xanthate is treated with an acid formaldehyde solution. Bath contained 6.0% H_2SO_4 , 17.5% Na_2SO_4 , and 0.5% $HCHO$. The temperature was 22.5°C.

short time interval, and then more slowly. Upon plotting $\log A$ versus t , the curve shows a rapid drop followed by a long-lived linear portion, as presented in Figure 2. The first steep portion apparently is associated with the decomposition of cellulose xanthic acid. A xanthate film was run with the same bath but without formaldehyde in order to determine

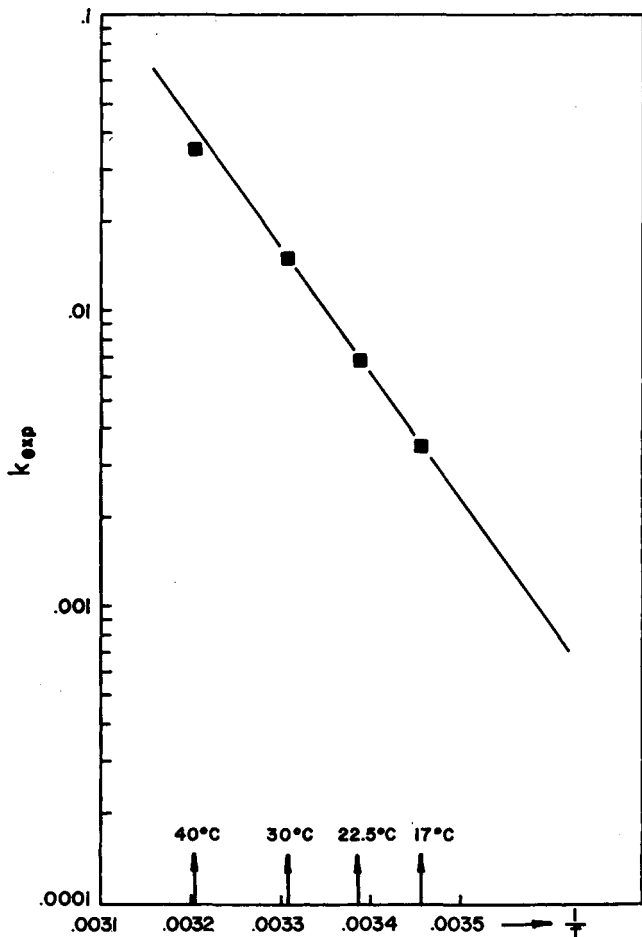


Fig. 3. Influence of temperature on the experimental decomposition rate k of *S*-hydroxymethyl cellulose xanthate.

the time required for the absorbance due to cellulose xanthic acid essentially to disappear. This time interval was less than 5 min., except at temperatures less than 15°C. or at pH >2. The slowly decomposing species can be shown to be the *S*-hydroxymethyl cellulose xanthate by plotting the spectrum at any time after the curve reaches the straight portion. The equation of the straight portion of the curve is

$$A = \alpha e^{-kt} \quad (2)$$

where A is the absorbance at time t and k is the experimental decomposition rate constant. The intercept of the straight line extrapolated to zero time (α) can be used to calculate the maximum possible fraction f of the xanthate that could have been converted to the formaldehyde derivative.

Effect of Temperature

The effect of temperature on the acid decomposition of the formaldehyde derivative was studied by reacting the viscose film with a bath containing 5.15% H_2SO_4 , 17.5% Na_2SO_4 , and 0.5% HCHO at several temperatures, and determining k , the slope of the straight line portion of the $\log A$ versus t plot. The logarithm of k versus $1/T$ is given in Figure 3. The slope of the straight portion of the curve, $\Delta E_a/R$, was calculated, and the activation energy was found to have a value of about 18,600 cal./mole.

Influence of Formaldehyde Concentration

To study the effect of formaldehyde on the formation and decomposition of the *S*-hydroxymethyl cellulose xanthate, a series of experiments was run with baths containing 5.15% H_2SO_4 , 17.5% sodium sulfate, and formaldehyde concentrations of 0.1–1.0%. At each concentration, a number of samples were run and the mean and standard deviation of the decomposition rate constant determined. The data obtained are given in Figure

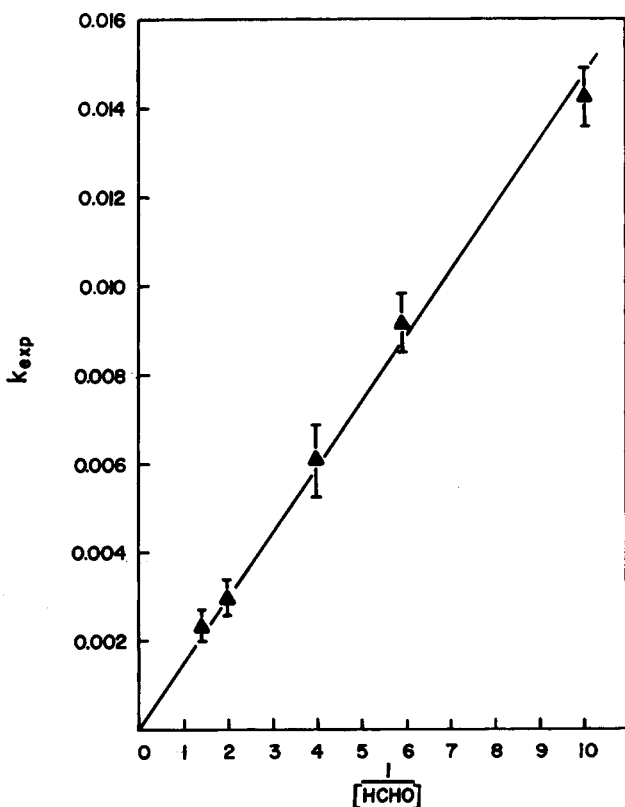


Fig. 4. Plot of the relation between the experimental decomposition rate and the formaldehyde concentration.

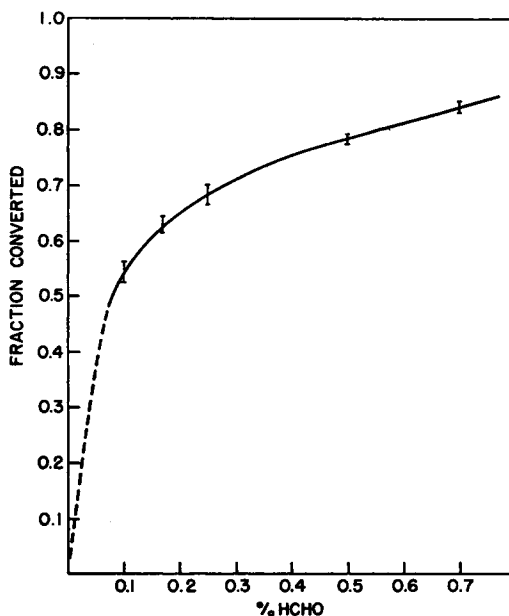


Fig. 5. Relation between the apparent maximum fraction of sodium cellulose xanthate converted to the derivative and the formaldehyde concentration.

4, which shows that the decomposition rate is inversely proportional to the formaldehyde concentration. Each point is given by a line which includes plus and minus the standard deviation.

The decomposition curves obtained in the above work were extrapolated to zero time, and the apparent maximum fractions converted to the formaldehyde derivatives were calculated. These data are plotted in Figure 5. The points are given as plus and minus one standard deviation. No satisfactory mathematical relationship has been found which is in agreement with the experimental data.

Influence of Acid Concentration

Experiments were run in which spinning baths containing 1–10% H_2SO_4 , 17.5% sodium sulfate, and 0.5% formaldehyde were reacted with the viscose film. The data compiled in Table I are the results of these experiments. It should be pointed out that the actual hydrogen ion concentration varies only slightly in these experiments due to the effect of the high salt concentration. The conclusions reached were that varying the acid concentration in the commercial spin bath had essentially no effect on the decomposition rate constant.

The value of the maximum fraction converted to *S*-hydroxymethyl cellulose xanthate increased with increasing acid concentration. No explanation for this is evident at present.

TABLE I

Effect of Acid on the Amount of *S*-Hydroxymethyl Cellulose Xanthate Found and Its Acid Decomposition

Acid concn., %	Number of experiments	k , min. ⁻¹	Fraction converted
1.00	5	0.0068	0.561
5.15	5	0.0069	0.585
7.43	9	0.0058	0.685
10.00	5	0.0066	0.803

TABLE II

Effect of pH on the Formation and Decomposition of *S*-Hydroxymethyl Cellulose Xanthate (Formaldehyde Concentration 0.5%)

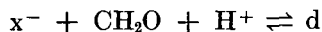
pH	Number experiments	k_{303} , min. ⁻¹	k_{280} , min. ⁻¹	$[x^-]/[d]$
1.0	11	—	0.0071	—
2.2	8	—	0.0070	—
3.5	7	0.0045	0.0044	0.45
4.0	7	0.0036	0.0042	0.68

Sodium acetate-acetic acid and KCl-HCl buffer systems were used for studies in the acid pH range. A summary of the calculated results is given in Table II. At pH > 3, data taken after 30 min. were used since linearity (as in Fig. 2) is not attained before that time.

In the higher pH range both xanthate ion and the formaldehyde derivative are present at the same time with no evidence of any other species which absorbs in this region being present. Measurements were therefore made of the experimental decomposition rate for each of these two species. The fact that they are within experimental error of being equal indicates that the system approaches equilibrium and suggests the use of equilibrium equations in the mechanism analysis.

The concentration ratio of xanthate, $[x^-]$, to the formaldehyde derivative, $[d]$, is also constant for a given set of conditions if equilibrium exists. The ratio can thus be calculated by using simultaneous equations.

Assuming the equation⁸ for the formation of the formaldehyde derivative is



the equilibrium is given by eq. (3):

$$K = [d]/[x^-][\text{CH}_2\text{O}][\text{H}^+] \quad (3)$$

With this relation and the value of $[x^-]/[d]$ at pH 3.5 (cf. Table II) a value for K of $10^{4.6}$ was obtained. At pH 4.0, K was $10^{5.0}$. These values

for K compare favorably with the value of $10^{5.2}$ found for the formaldehyde derivative of ethyl xanthate by Thumm and Tryon.⁸

Effect of Zinc Ion

A zinc cellulose xanthate film was formed by reacting an ion-exchanged viscose film with 5% zinc sulfate solution. This film was then treated with a solution containing 5.15% H_2SO_4 , 17.5% Na_2SO_4 , and 0.5% formaldehyde. A spectrum run immediately after the addition of the formaldehyde solution indicated the presence of only *S*-hydroxymethyl cellulose xanthate. In another experiment ion exchanged viscose was treated with a solution containing 6.5% H_2SO_4 , 15% Na_2SO_4 , 7% $ZnSO_4$, and 0.5% formaldehyde. Under these conditions, only the formaldehyde derivative was detected. These results suggest that the formaldehyde derivative is readily formed from zinc cellulose xanthate. Further preliminary data indicated that, under these conditions, the presence of zinc does not have an appreciable effect on either the fraction of the original xanthate converted into the formaldehyde derivative or its acid decomposition rate.

CONCLUSIONS

The following conclusions can be drawn from this work.

(1) In acid media, formaldehyde reacts reversibly with the xanthate groups in cellulose xanthate to form a new compound.

(2) The ultraviolet spectrum of the formaldehyde derivative is similar to that of *S*-methyl cellulose xanthate. The absorption maximum is at 280 $m\mu$ and the extinction coefficient is 11,600.

(3) The stability of the formaldehyde derivative in the presence of water is much greater than that of the xanthate ion or xanthic acid provided that any excess of formaldehyde and acid is maintained in the system.

(4) The aqueous acid decomposition of the formaldehyde derivative apparently follows pseudo first-order kinetics.

(5) The experimental rate constant for the decomposition of the formaldehyde derivative is inversely proportional to the formaldehyde concentration.

(6) At low pH the apparent maximum conversion to the formaldehyde derivative increases with the formaldehyde concentration.

(7) At high acid concentrations there is little or no effect of acid concentration on the decomposition rate of the derivative.

(8) At low acid concentration the rate of decomposition decreases with decreasing hydrogen ion concentration.

(9) The activation energy for the decomposition of the formaldehyde derivative is 18,600 cal./mole.

(10) An equilibrium constant of about $10^{4.8}$ is calculated from concentration data for the reaction: xanthate + $HCHO + H^+ \rightleftharpoons$ derivative.

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Résumé

La formaldéhyde réagit réversiblement avec le xanthate de cellulose en solution acide pour former un produit présentant un maximum d'absorption à 280 m μ et un coefficient d'extinction de 11,600. La fraction primitive de xanthate transformée en formaldéhyde est reliée à la concentration en formaldéhyde. La vitesse de décomposition en milieu acide du dérivé du formaldéhyde est du pseudo premier ordre et est inversément proportionnelle à la concentration en formaldéhyde. Pour des concentrations élevées en acide, la vitesse de décomposition est indépendante de la concentration en acide, mais la vitesse diminue lorsque l'acidité diminue dans le domaine de pH de 1 à 4. A partir des résultats obtenus par cette étude, on trouve que la constante de formation du dérivé du formaldéhyde est de l'ordre de 10^{4.8}. L'énergie d'activation pour la décomposition du dérivé du formaldéhyde est de 18,600 calories/mole.

Zusammenfassung

Formaldehyd reagiert mit Cellulosexanthat in wässriger Säurelösung reversibel unter Bildung eines Produkts mit einem Absorptionsmaximum bei 280 m μ und einem Extinktionskoeffizienten von 11,600. Der Bruchteil des zur Formaldehydform umgewandelten Xarthat wird zur Formaldehydkonzentration in Beziehung gesetzt. Die Zersetzungsgeschwindigkeit des Formaldehydderivats in wässriger Säure ist von pseudoerster Ordnung und der Formaldehydkonzentration verkehrt proportional. Bei hoher Acidität ist die Zersetzungsgeschwindigkeit von der Säurekonzentration unabhängig, sie nimmt jedoch im pH-Bereich 1 bis 4 mit fallender Acidität ab. Unter Verwendung der in dieser Untersuchung erhaltenen Daten wurde die Gleichgewichtskonstante für die Bildung des Formaldehydderivates in der Grössenordnung 10^{4.8} berechnet. Die Aktivierungsenergie der Zersetzung des Formaldehydderivates beträgt 18,600 cal/mol.

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