Mechanism for the Aqueous Acid Decomposition of the Formaldehyde Derivative of Cellulose Xanthate

LYLE H. PHIFER, JAMES P. DUX, LELAND B. TICKNOR, and M. THOMAS O'SHAUGHNESSY,* *American Viscose Division, FMC Corporation, Marcus Hook, Pennsylvania*

Synopsis

Kinetic equations for the decomposition of S-hydroxymethyl cellulose xanthate in the presence of acid and formaldehyde are derived. The assumed mechanism involves an equilibrium between the S-hydroxymethyl cellulose xanthate and cellulose xanthic acid and xanthate ion. Decomposition appears to proceed via interaction between the cellulose xanthate ion and hydrogen ion which form an activated complex that subsequently decomposes to cellulose and carbon disulfide. The equations derived show the proper dependence on acid and formaldehyde concentrations. An estimate of the equilibrium constant between cellulose xanthate and S-hydroxymethyl cellulose xanthate is calculated from the rate constants.

INTRODUCTION

In a previous paper[1] the ultraviolet absorption spectrum and the extinction coefficient for the formaldehyde derivative of cellulose xanthate was given. The rate of decomposition of this derivative in aqueous acid was shown to be affected by acid concentration, formaldehyde concentration and temperature. This paper will present a proposed mechanism for this decomposition.

Any such mechanism must be consistent with the following facts.

(1) The major portion of the decomposition follows pseudo first-order kinetics.

(2) At high acid concentrations, pH <1, the decomposition rate is independent of acid concentration, while in the pH range 1–4, the experimental rate constant decreases with decreasing acid concentration.

(3) At high acid concentrations, the decomposition rate is inversely proportional to the formaldehyde concentration.

(4) The formation of the derivative is a reversible reaction and a pseudo equilibrium exists when cellulose xanthate is in contact with an aqueous acidic formaldehyde solution. The equilibrium is not fully established due to the observed decomposition.

(5) The work of Thumm and Tryon[2] on the formation, isolation, and characterization of the formaldehyde derivative of ethyl xanthate indicates

* Present address: Aerospace Corporation, Los Angeles, California.

that the stoichiometry of the reaction involves one xanthate ion, one formaldehyde molecule and one hydrogen ion to form a nonionized product having the formula $C_2H_5OCS_2CH_2OH$, which may be called the S-hydroxy-methyl ethyl xanthate. The work[1] on cellulose xanthate indicates a corresponding product is formed.

MECHANISM

Decomposition Mechanism

In consideration of the above facts, the following equilibrium appears to be the simplest reaction that can be written for the formation of the derivative, which may be called S-hydroxymethyl cellulose xanthate

$$\text{Cell—OCS}_2^- + \text{H}_3\text{O}^+ + \text{CH}_2\text{O} \rightleftharpoons \text{CellO—CS}_2\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \qquad (1)$$

In competition with this reaction is the formation of the cellulose xanthic acid:

$$\text{Cell—OCS}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{Cell—OCS}_2\text{H} + \text{H}_2\text{O} \qquad (2)$$
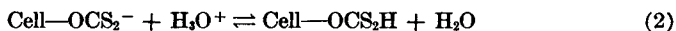
Although reaction (1) indicates molecular formaldehyde as the reactant, several different species of formaldehyde may be present in aqueous solution. Bieber and Trumpler[3] have shown that the hydrated or methylene glycol form predominates in aqueous solutions, and Wadano[4] has suggested that in acid solution the cation, CH_2OH^+, is formed. Also, the reaction of these various forms of formaldehyde with xanthic acid is a possibility. However, since the interest here is in the decomposition of the derivative and, since the various species of formaldehyde as well as xanthate are in rapid equilibria with each other, it is irrelevant which species is written in the formation reactions.

Since the above reactions are reversible, the decomposition of the derivative could take place via the xanthate ion, xanthic acid, or the S-hydroxymethyl xanthate itself. However, the fact that the decomposition rate is inversely proportional to the formaldehyde concentration at high acid concentrations, where essentially all of the xanthate is in the derivative form, indicates that the derivative itself does not decompose directly to cellulose but decomposition proceeds by reversal of reaction (1) and subsequent acid decomposition of the cellulose xanthate. Also, the fact that acid concentration has little effect on the rate of decomposition at high acid levels would not be expected if the decomposition proceeded via the derivative.

Lewis[5] and Klein and co-workers[6] have proposed that the acid decomposition of xanthate takes place via an activated complex formed between xanthate ion and hydrogen ion, which is structurally different from xanthic acid. It seems reasonable that our mechanism should be consistent with this and we will follow the scheme used by Klein. Thus, decomposition is by reversal of reaction (1) followed by

$$\text{Cell—OCS}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{XH*} \rightarrow \text{Cellulose} + \text{CS}_2 \qquad (3)$$
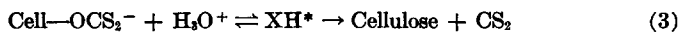
where XH* is the activated complex described by Lewis[5] and Klein et al.[6]

The proposed mechanism for the formation and decomposition of S-hydroxymethyl cellulose xanthate is given by reactions (1), (2), and (3). It should be pointed out that the data could be equally well interpreted as a reaction between xanthic acid and formaldehyde.

The logarithmic dependence of the absorbance at 280 mμ with time indicates pseudo first-order decomposition kinetics. This in turn implies that the equilibria illustrated by reactions (1) and (2) are very rapid in comparison with the rate of decomposition given by reaction (3). The concentrations of formaldehyde and hydronium ion within the gel film phase will remain constant during a run,[7] since they are proportional to their concentrations in the bath, which will act as a large reservoir. On the other hand, the concentration of xanthate and derivative will change with time since the total amount of these species present is small. This large relative excess of formaldehyde and acid explains the pseudo first-order kinetics observed.

Mathematical Development

To show that the proposed mechanism is consistent with the observed kinetics, it is necessary to derive the expression for the rate in terms of the observed variables. Since it is assumed that the reversible reactions (1), (2) and (3) are rapid compared to the decomposition, the equilibrium expressions may be written

$$K_a = [\text{H}^+][\text{X}^-]/[\text{XH}] \tag{4}$$

$$K_F = [\text{D}]/[\text{X}^-][\text{H}^+][\text{F}] \tag{5}$$

$$K^* = [\text{XH}^*]/[\text{H}^+][\text{X}^-] \tag{6}$$

which have been simplified by using concentrations instead of activities. [D] represents the concentration of the formaldehyde derivative, [XH] that of the xanthic acids, and [F] the formaldehyde concentration.

Since the proposed mechanism assumes a state approaching equilibrium for the several xanthate species, the rate equation for decomposition must include them all

$$\frac{d}{dt}([\text{X}^-] + [\text{XH}^*] + [\text{XH}] + [\text{D}]) = -k[\text{XH}^*] \tag{7}$$

The equilibria (4), (5), and (6) are used to express the concentrations of the xanthate species in terms of D and the final rate equation is

$$d \ln D/dt = -kK^*/\{(1/[\text{H}^+]) + K^* + (1/K_a) + K_F[\text{F}]\} \tag{8}$$

Thus, the proposed mechanism predicts pseudo first-order kinetics. The experimental rate constant is given by

$$k_{\text{exp}} = kK^*/\{(1/[\text{H}^+], + K^* + (1/K_a) + K_F[\text{F}]\} \tag{9}$$

which reduces to

$$k_{\text{exp}} = kK^*/\{(1/[\text{H}^+]) + (1/K_a) + K_F[\text{F}]\} \tag{10}$$

if we assume K^* is small compared to the other terms in the denominator on the right-hand side of eq. (9).

DISCUSSION

If the formaldehyde concentration is zero, eq. (10) reduces to

$$k_{exp}^H = kK^*/\{(1/[H^+]) + (1/K_a)\} = kK^*K_a[H^+]/(K_a + [H^+]) \quad (11)$$

which is the expression Klein and co-workers[6] found for the acid decomposition of xanthate, neglecting activity coefficients.

In the previous paper[1] it was shown that K_F is of the order of 10^5. Klein[6] has given a value of K_a for ethyl xanthate of $10^{-1.6}$. It may be assumed that cellulose xanthate has a similar acid constant. Under these conditions, the term involving K_a in the denominator of eq. (10) is small compared to the term involving K_F, provided the formaldehyde concentration is greater than about $0.1M$. With these approximations, eq. (10) reduces to

$$k_{exp} = kK^*/\{(1/[H^+]) + K_F[F]\} \quad (12)$$

For pH $\leq$ 1 and [F] $\geq$ 0.1

$$k_{exp} = kK^*/K_F[F] \quad (13)$$

while for pH $\geq$ 5 and [F] $\leq$ 0.1

$$k_{exp} = kK^*[H^+] \quad (14)$$

Thus, the mechanism is consistent with the observed effects of acid and formaldehyde concentration on the decomposition rate.

If the expression for the rate constant in the absence of formaldehyde [eq. (11)] is divided by that for the rate constant in the presence of formaldehyde [eq. (10)], the ratio obtained is

$$\frac{k_{exp}^H}{k_{exp}} = 1 + \frac{K_a K_F[F]}{1 + (K_a/[H^+])} \quad (15)$$

In strong acid solutions ($[H^+] > 0.1$) with formaldehyde concentrations greater than $0.1M$, this reduces to

$$k_{exp}^H/k_{exp} = K_a K_F[F] \quad (16)$$

Thus, since $K_a K_F$ is about 10^3, if [F] is 0.1, a hundredfold decrease in the rate of xanthate decomposition is observed. This factor remains approximately constant as the acid concentration is decreased, until a pH of about 2 is reached, when the effect of formaldehyde is progressively less. At pH greater than 5 the formaldehyde has practically no effect since, under these conditions, very little of the derivative is formed.

The equilibrium constant of the derivative may be estimated from the rate expression at high and low acid concentrations, assuming the formalde-

hyde concentration to be unchanged and greater than $0.1M$.   At low pH ($<$1), eq. (10) reduces to

$$k^0 = kK^*/K_F[F]$$

(17)

and at high pH (3–4)

$$k' = kK^*/(1/[H^+]) + K_F[F]$$

(18)

from which

$$K_F = \left(\frac{k'}{k^0 - k'}\right) \frac{1}{K_a[F][H^+]}$$

(19)

where [H$^+$] refers to the hydrogen ion concentration in the high pH experiment.   Using the rate constants given in the previous report[1] of 0.00713 and 0.00419 at pH 1 and 4, respectively, we calculate

$$K_F = 10^{4.8}$$

(20)

This is in excellent agreement with the value of $10^{4.8}$ and $10^{5.0}$ calculated in the previous paper[1] from concentration measurements.

References

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Résumé

On a déduit les équations cinétiques correspondant à la décomposition du xanthate de S-hydroxyméthyl-cellulose en présence d'acide et de formaldéhyde.   Le mécanisme supposé consiste en un équilibre entre le xanthate de S-hydroxyméthyl-cellulose, l'acide cellulose xanthique et l'ion xanthate correspondant.   Il semble que la décomposition se fasse par une interaction entre l'ion cellulose xanthate et l'ion hydrogène qui forment un complexe activé qui se décompose ultérieurement en cellulose et sulfure de carbone.   Les équations déduites révèlent la dépendance adéquate des concentrations en acide et formaldéhyde.   On a évalué la constante d'équilibre entre xanthate de cellulose et xanthate de S-hydroxyméthyl-cellulose.

Zusammenfassung

Es werden kinetische Gleichungen für die Zersetzung von S-Hydroxymethylzellulosexanthat in Anwesenheit von Säure und Formaldehyd abgeleitet.   Es wird ein Mechanismus mit einem Gleichgewicht zwischen S-Hydroxymethylzellulosexanthat, Zellulose, Zellulosexanthogensäure und Xanthation angenommen.   Die Zersetzung

scheint über eine Wechselwirkung zwischen dem Zellulosexanthation und dem Wasserstoffion zu verlaufen, die einen aktivienten Komplex bilden, der sich sodann in Zellulose und Schwefelkohlenstoff zersetzt. Die abgeleiteten Gleichungen zeigen die richtige Abhängigkeit von Säure- und Formaldehydkonzentration. Ein Wert der Gleichgewichtskonstanten zwischen Zellulosexanthat und S-Hydroxymethylzellulosxanthat wird aus den Geschwindigkeitskonstanten berechnet.