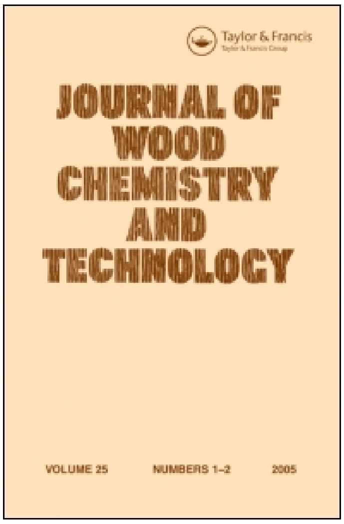

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KINETIC STUDY OF END-GROUP STABILIZATION IN HYDROCELLULOSE BY HYDROGEN SULFIDE[1]

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ABSTRACT

The rate of stabilization of hydrocellulose and glucose against alkaline degradation by hydrogen sulfide was studied as a function of pH and H_2S-concentration. The rate of this reaction increases to a maximum with an increase in pH from 3.5 to 6.3. The maximum rate is significantly enhanced by the presence of ammonia base. With increasing H_2S-concentration, the stabilization rate increases in a sigmoidal manner. It is demonstrated that this kinetic pattern is in full accordance with the reaction mechanism proposed by Procter[4] involving conversion to a thioalditol *via* a *gem*-dithiol intermediate.

INTRODUCTION

It has been shown that hydrocellulose as well as softwood glucomannans can be stabilized against alkaline degradation by treatment in hydrogen sulfide-sodium hydrosulfide buffered systems at elevated temperatures and pressures.[4-9] The stabilization appears to be based on the conversion of reducing end-groups to alkali-stable 1-thio-D-glucitol 2 moieties, as demonstrated by Procter[4] and *gem*-dithiols 1 are probable intermediates in the conversion as illustrated by equation (1).

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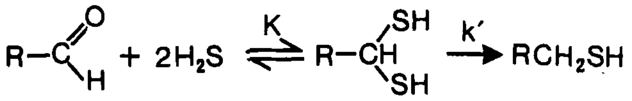


End groups 1 2 (1)

THEORY

Accepting the validity of Equation (1) as the mechanism of the stabilization reaction and assuming further that the establishment of the equilibrium between the reducing end-groups and the *gem*-dithiol 1 is instantaneous, the anticipated kinetic relationships can be derived in a straightforward manner. The equilibrium constant K can be expressed as

$$K = \frac{[INT]}{[RE]' \times [H_2S]^2} = \frac{[INT]}{\{[RE] - [INT]\} \times [H_2S]^2} \qquad (2)$$

where [INT] is the molar concentration of the intermediate-*gem*-dithiol 1. [RE] and [RE]' are the molar concentrations of the reducing end-groups initially and after the establishment of the equilibrium. Thus, the concentration of the intermediate can be derived from Equation (2).

$$[INT] = \frac{K \times [RE] \times [H_2S]^2}{1 + K \times [H_2S]^2} \qquad (3)$$

The rate of the formation of the stabilized end-group [SEG] 2 will be proportional to the concentration of the intermediate:

$$\frac{d[SEG]}{dt} = k' \times [INT] = k' \times \frac{K[H_2S]^2}{1 + K[H_2S]^2} \times [RE] \qquad (4)$$

where [SEG] is the concentration of the stabilized end-group (1-thio-D-glucitol group 2) and k' is constant.

If hydrogen sulfide is present in sufficient excess, its concentration remains essentially constant and

$$k' \times \frac{K[H_2S]^2}{1 + K[H_2S]^2} = k = \text{constant} \qquad (5)$$

Under these conditions, the overall conversion to stabilized end-groups becomes a first order reaction in respect to the concentration of the reducing end-groups:

$$\frac{d[SEG]}{dt} = k[RE] \qquad (6)$$

$$\text{and } \ln\frac{[RE]_o}{[RE]} = \ln\frac{[RE]_o}{[RE]_o - [SEG]} = kt \qquad (7)$$

where $[RE]_o$ is the original molar concentration of the reducing end-groups.

The relationship between the observed rate constant k and the concentration of hydrogen sulfide is expressed by Equation (5) which can be rearranged in the following form

$$\frac{1}{k} = \frac{1}{k'K} \times \frac{1}{[H_2S]^2} + \frac{1}{k'}, \qquad (8)$$

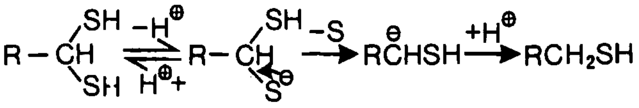
This equation indicates that a plot of the inverse of the observed rate constant versus the inverse square of hydrogen sulfide concentration should give a straight line intercepting the 1/k - axis at the value 1/k' from which the magnitude of k' can be determined.

Equations (1) to (8) are, of course, equally valid for the conversion of monomeric glucose to 1-thio-D-glucitol, providing the underlying assumptions are correct. In this case, the observed rate constant k pertains to Equation (9).

$$\ln\frac{[G]_o}{[G]} = k\ t \qquad (9)$$

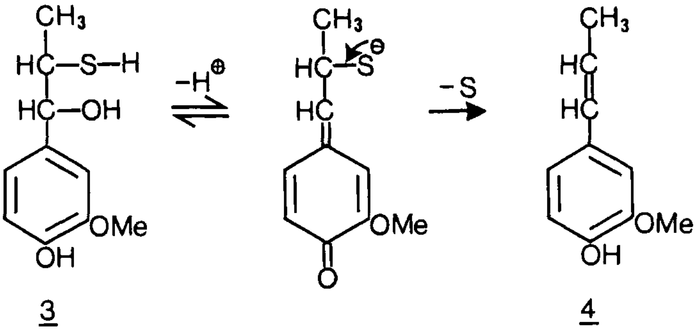
where $[G]_o$ and [G] are the concentrations of glucose at zero- and time t, respectively.

The contemplated mechanism and derived equations provide no explanation, however, for the fact that the stabilization rate of hydrocellulose drops significantly as the pH of the reaction medium is reduced below 6 as demonstrated by Procter and Apelt.[7] To account for this effect, the possibility should be considered that the conversion of the gem-dithiol to 1-thioalditol may occur via the monoanion of the former compound.



$$R-CH(SH)_2 \underset{H^{\oplus}+}{\overset{-H^{\oplus}}{\rightleftharpoons}} R-CH(SH)S^{\ominus} \xrightarrow{-S} R\overset{\ominus}{C}HSH \xrightarrow{+H^{\oplus}} RCH_2SH \qquad (10)$$

In support of this hypothesis, an analogous reaction has been observed in connection with lignin model compound studies.[10,11] It was shown that 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanethiol 3 was converted to isoeugenol 4 through the ionization of thiol groups and the release of elemental sulfur:



To test the validity of the outlined ideas the following studies were carried out:

a. Kinetic studies using both hydrocellulose and glucose as substrates to establish the correctness of Equations (7) and (9).

b. Kinetic studies using glucose as substrate at varying pH-values to test the mechanism expressed by Equation (10). Both sodium- and ammonium bases were used in these studies.

c. Studies on hydrocellulose using ammonia base and varying the concentration of hydrogen sulfide in order to establish the correctness of Equation (8).

EXPERIMENTAL

Preparation and Alkaline Degradation of Hydrocellulose

Hydrocellulose was prepared by hydrolyzing purified cotton cellulose[12] with 2.5 N HCl (acid/cellulose = 30/1 by weight) at 60°C under N_2 for 2 hours. The complete alkaline peeling of this hydrocellulose by 5% NaOH at 100°C resulted in a weight loss of 32.5% which decreased to 6.4% after reaction with $NaBH_4$[13] or with H_2S in combination with ammonia, as shown in Figure 1. Presumably, this 6.4% loss was caused by the direct dissolution of the oligomeric material in the hydrocellulose during the alkaline degradation reaction. Therefore, the complete alkaline peeling loss (L) of the original hydrocellulose was actually 32.5-6.4% = 26.1% from which $[RE]_o$, the mole fraction of original reducing end-groups (in Equation 7), can be obtained according to Equation (11)[14]

$$[RE]_o = \frac{L - 6.4}{X_n \times 100} \qquad (11)$$

where Xn is the average degradable chain length which equals 68 glucose units in case of hydrocellulose.[14]

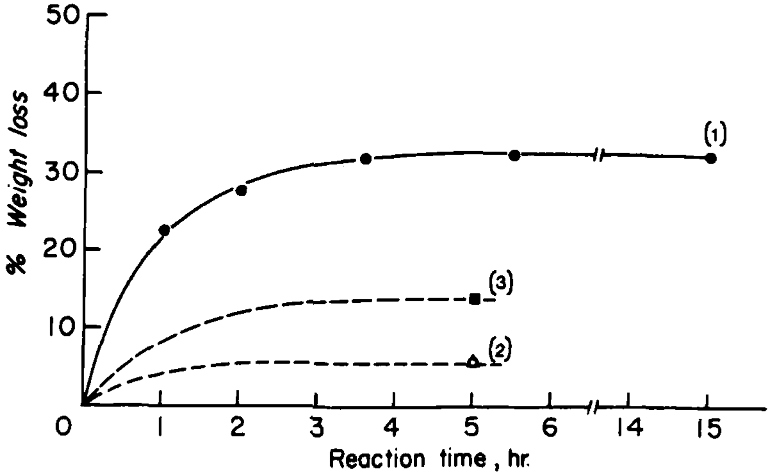


FIGURE 1. Alkaline degradation of hydrocellulose in 5% NaOH at 100°C. Curve (1): Original hydrocellulose. Curve (2): Borohydride reduced hydrocellulose or H_2S-base treated hydrocellulose. Curve (3): Hydrocellulose, partially stabilized in a H_2S-NH_4OH system.

Stabilization of Hydrocellulose

Stabilization of hydrocellulose was carried out in 45 ml Parr autoclaves. Hydrogen sulfide gas under pressure was introduced into the autoclaves containing hydrocellulose (0.5 g OD weight) and ammonium- or sodium hydroxide solution (25 ml). Mechanical mixing of the suspension was maintained during this process until the hydrogen sulfide partial pressure in the autoclave reached the equilibrium as indicated by a high precision pressure gage (Matheson #63-5622). The molar concentration of the hydrogen sulfide solution at ambient temperature was derived from the measured partial pressure of hydrogen sulfide according to a modified equation established originally by Shih et al.[15]

$$\mathrm{Log}\ pH_2S = 4.6962 - 724.0/T + \mathrm{Log}\ C$$

where

pH_2S = H_2S partial pressure, psi

T = temperature,°K

C = H_2S concentration in solution, mole/l.

Subsequently, the autoclaves were sealed and inserted in a rocking cylindrical aluminum block preheated to the appropriate temperature. The heating of the block was controlled by a linear temperature programmer and monitored by a thermocouple inserted into the heating block. The temperature inside the autoclave was measured by a separate thermocouple connected with a digital thermometer and remained constant within 0.2°C. The zero reaction time, in each case, was recorded at a point at which the autoclaves had reached the selected reaction temperature indicated by the digital thermometer. In each series of experiment, the heat-up time was controlled to be 8 minutes.

After the stabilization reaction, the autoclave was dipped in ice water and the hydrocellulose was washed thoroughly with distilled water through suction and air dried. No weight loss or lowering of the $\overline{DP}_n$ (number average degree of polymerization) of the hydrocellulose at this stage was found (for example, the $\overline{DP}_n$ of the original hydrocellulose measured in cadoxen was 290 and did not change after the hydrocellulose was treated with 150 psi H_2S and 0.004 N NH_4OH for 14 hours at 140°C). In order to obtain the mole fraction of unstabilized reducing end-groups ($[RE]_o-[SEG]$ in Equation (7)), the treated hydrocellulose was then subjected to the alkaline degradation with 5% NaOH at 100°C for 5 hours. After the degradation reaction, the suspension was acidified and filtered, the hydrocellulose was washed with 1% acetic acid, followed by water and air-dried. A moisture determination was made and weight loss (WL) calculated. Figure 2 shows the weight loss (WL) of partially stabilized hydrocellulose during the alkaline degradation reaction as a function of the stabilization reaction time at 160°C. Similarly, WL's were obtained for those stabilization reactions carried out at 140° and 120°C. After subtracting 6.4% from WL to account for the dissolved oligomeric material, the $[RE]_o-[SEG]$ is then obtained according to the following equation.

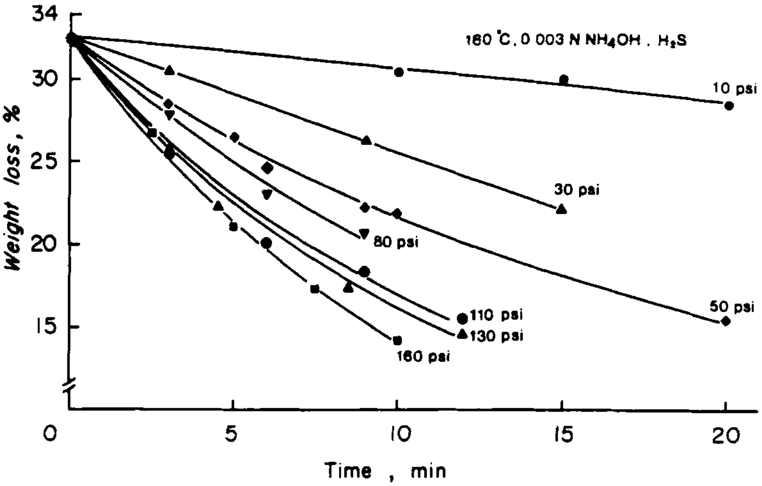


FIGURE 2. Alkaline degradation of partially stabilized hydrocellulose after 5 hours in 5% NaOH at 100°C as function of the reaction time in stabilization. Stabilization was carried out under H_2S-pressure (as indicated) and constant concentration of NH_4OH at 160°C.

$$[RE]_\circ - [SEG] = \frac{WL-6.4}{X_n \times 100} \qquad (12)$$

Thus equation (7) can be represented by:

$$\ln \frac{[RE]_\circ}{[RE]} = \ln \frac{26.1}{WL-6.4} = kt \qquad (13)$$

Stabilization of D-glucose

The conversion of D-glucose to 1-thio-D-glucitol was determined by measuring, colorimetrically, the unreacted D-glucose in the solution after the treatment with H_2S-sodium- or ammonium hydroxide solutions with the phenol-sulfuric acid method.[16]

To the reactor containing 20 ml of D-glucose solution (1 to 1.5 mM) with the presence of either NaOH or NH_4OH, the hydrogen sulfide gas was introduced by the same procedure as described in the previous section. At the end of the stabilization reaction, the reactor was cooled down rapidly and the solution was acidified to pH ∿ 2 with 1N HCl. The precipitated sulfur was filtered, washed with distilled water and the combined filtrate was concentrated in a rotatory evaporator. The concentrated sugar solution was then adjusted to 25 ml with distilled water. At this stage, the solution was slightly turbid. A 2 ml aliquot was taken and adjusted to 10 ml with 95% ethanol to obtain a clear solution from which 2 ml was used for the colorimetric determination. A calibration curve was constructed according to Dubois *et al.*[16] The standard solution consisted of 95% ethanol and distilled water (4 to 1, by volume), containing 5 to 50 mg/l of D-glucose. Typical experimental runs are illustrated in Figure 3.

RESULTS AND DISCUSSION

Kinetics of Stabilization by H_2 S in NaOH- and Ammonia Systems

The hydrocellulose sample used in the study lost 32.5% of its weight in complete alkaline peeling. By borohydride reduction the peeling loss was reduced to 6.4%. This remaining weight loss is

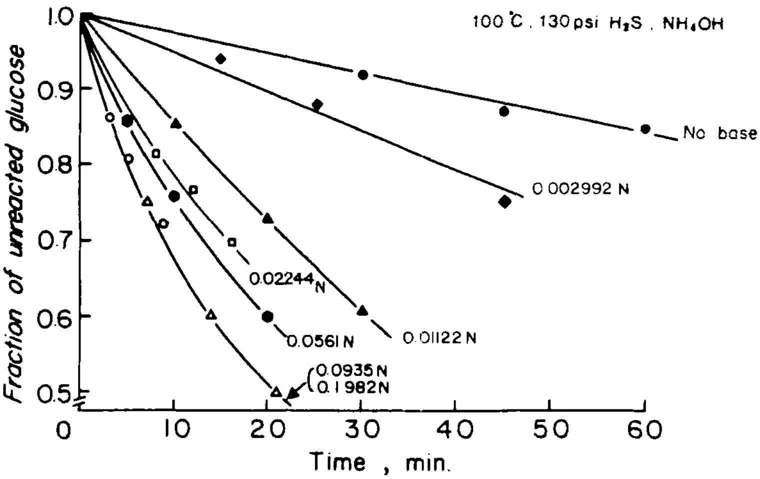


FIGURE 3. Fraction of unreacted glucose as function of the reaction time in stabilization. Stabilization was carried out at 100°C with constant H_2S-pressure and various concentrations of NH_4OH (as indicated).

probably not due to incomplete stabilization of end-groups but is likely to be caused by the dissolution of oligomeric cellulose hydrolysis products in the alkaline medium.

Confirming the results by Procter and Apelt,[7] complete stabilization of the hydrocellulose could be achieved by heating the sample at 130°C in 0.05 N aqueous alkali under H_2S-pressure, as shown in Figure 4. The completeness of the process was independent on whether NaOH or ammonia was used as the base. In absence of base, however, the stabilization process was strongly retarded.

To obtain kinetic data for the stabilization process, the unreacted reducing end-groups in partially stabilized samples were measured from the weight loss observed in alkaline peeling (See Experimental Section). It was found that regardless of H_2S-pressure applied, the data conformed to the first-order relationship predicted by Equation (7), as illustrated in Figure 5. The same figure also suggests that the stabilization

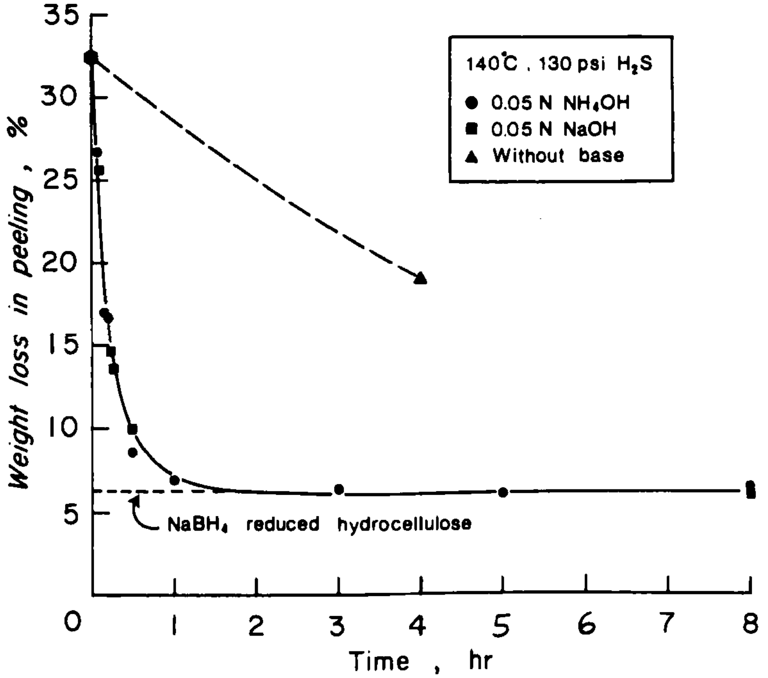


FIGURE 4. Alkaline degradation of completely and partially stablized hydrocellulose after 5 hours in 5% NaOH at 100°C as function of the reaction time in stabilization.

rate is slightly but significantly higher when ammonia instead of sodium hydroxide is used as the base.

The conversion of glucose to 1-thio-D-glucitol is a much faster reaction than the stabilization of reducing end-groups in hydrocellulose and could be studied at 100°C reaction temperature. In kinetic runs, the remaining unreacted glucose was determined using the well-known phenol-sulfuric acid[16] reaction. Again, the rate data fit well with a first order relationship (Figure 6), in conformity with Equation (9). Another similarity with the hydrocellulose kinetics was the higher reaction rate observed in ammonia systems.

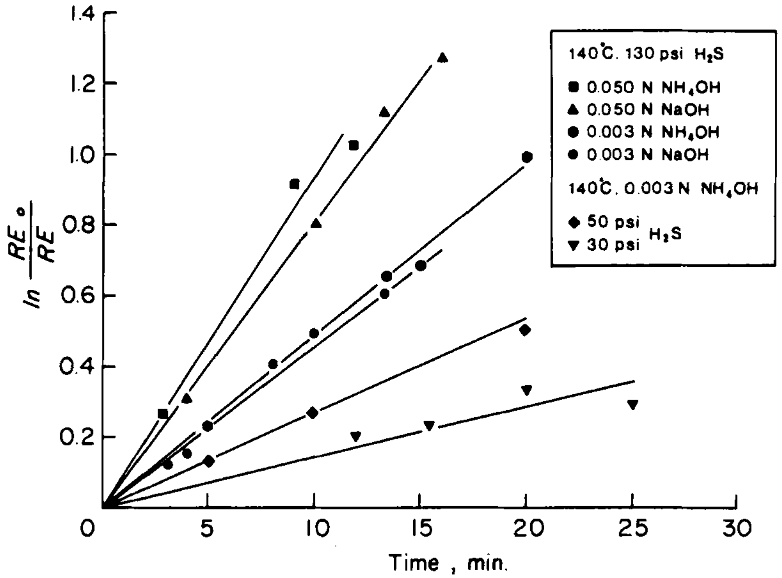


FIGURE 5. First-order rate plots for the stabilization of hydrocellulose in H_2S-base systems at 140°C.

Effect of Initial Base Concentration on the Rate of Reaction

For the purpose of determining the influence of the base concentration on the rate of stabilization under constant H_2S-pressure it was more convenient to use glucose rather than hydrocellulose as the substrate. Both NaOH- and ammonia concentrations were varied in the range from zero to 0.2 M and the first order rate constants determined under 130 psi hydrogen sulfide pressure at 100°C. The results obtained are shown in Figure 7 and demonstrate that increases in both NaOH- and ammonia concentrations from zero to .05 M accelerate the rate by more than ten-fold but further increases in base concentration are practically without effect. However, the maximum rate observed in ammonia systems exceeds by approximately 30% that of NaOH systems.

In order to determine the effect of pH on the rate in sodium-

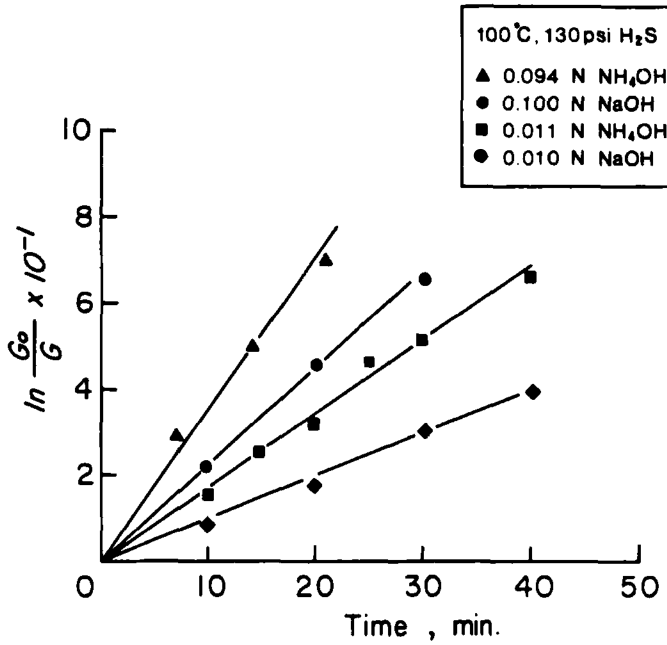


FIGURE 6. First-order rate plots for the stabilization of D-glucose in H_2S-base systems at 100°C.

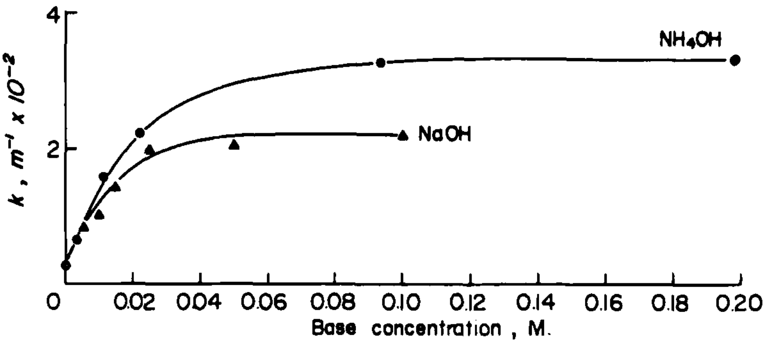


FIGURE 7. Dependence of observed rate constants for the stabilization of D-glucose on the base concentration. H_2S pressure: 130 psi. Temperature: 100°C.

and ammonia based systems, the pH-values were computed for individual runs from the available data on dissociation constants of NH_3 and H_2S and from the vapor-liquid equilibrium data for H_2S[15]. When the rate data, expressed as fractions of maximum rate, were plotted against computed pH-values, an identical curve was obtained for sodium- and ammonia based systems, as shown in Figure 8. The form of the curve is sigmoidal giving support to the idea that the conversion rate is indeed dependent on the concentration of the monoanion of gem-dithiol (Equation 10), if it is assumed that the pK-value of the first ionization of this compound is approximately 5.2.

It is more difficult, however, to explain the difference in the maximum rate between sodium- and ammonia based systems. It is not very likely that the rate constant k' would be different in both systems. Therefore, the difference between the maximum rates in these two systems would suggest that the instantaneous establishment of the equilibrium between the reducing end-groups and the gem-dithiols 1 occurs only in the ammonia based system. It has been shown, under below-neutral conditions, ammonia or

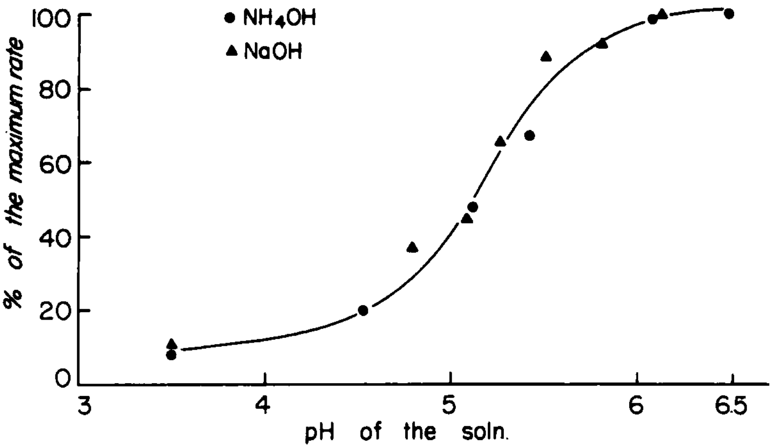


FIGURE 8. Effect of pH on the rate of the stabilization of D-glucose in the H_2S-base systems.

amine promotes the addition of hydrogen sulfide to simple carbonyl compounds yielding corresponding gem-dithiol derivatives.[17,18,19] This is probably caused by the condensation reaction between ammonia and carbonyl forming an activated immonium ion[20,21] which facilitates the nucleophilic addition of hydrogen sulfide.

Effect of Hydrogen Sulfide Concentration on Stabilization

At very low concentrations of H_2S, $1 >> K[H_2S]^2$, and consequently, Equation (4) approaches the form given by equation (14), suggesting an approximate second order rate relationship in respect to H_2S-concentration.

$$\frac{d[SEG]}{dt} = k'K\,[RE]\,[H_2S]^2 \qquad (14)$$

On the other hand, at sufficiently high H_2S-concentrations

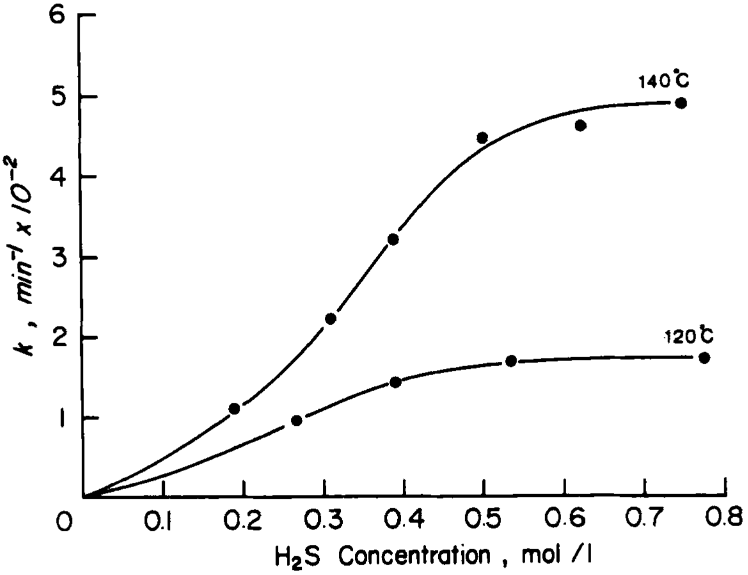


FIGURE 9. Relationship between the stabilization rate constant and the H_2S-concentration at 140° and 120°C with constant amount of NH_4OH (0.003 M).

$K[H_2S]^2 >> 1$ and Equation (4) becomes nearly equivalent to equation (15), expressing a zero-order relationship.

$$\frac{d[SEG]}{dt} = k' \times [RE] \qquad (15)$$

Consequently, if Equation (4) is valid for the stabilization process, a sigmoidal relationship can be anticipated between the rate of the stabilization and the concentration of hydrogen sulfide.

To test the validity of Equation (4), first-order rate constants for the stabilization of hydrocellulose with constant amount of ammonia (0.003 M) and various concentrations of H_2S were

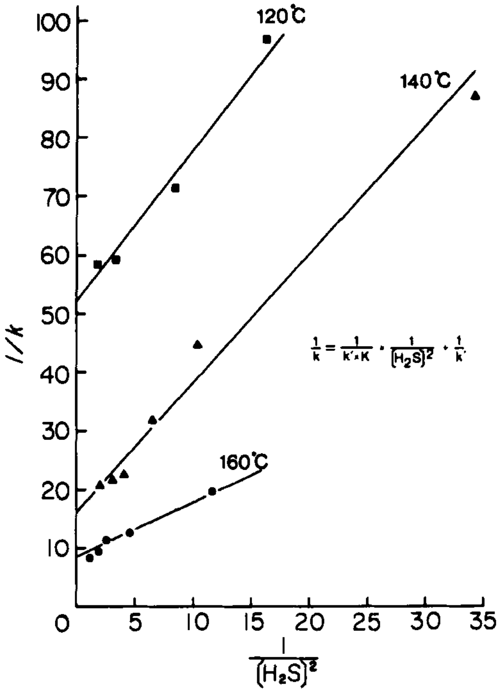


FIGURE 10. Relationship between k^{-1} and $[H_2S]^{-2}$ for the stabilization of hydrocellulose at various temperatures.

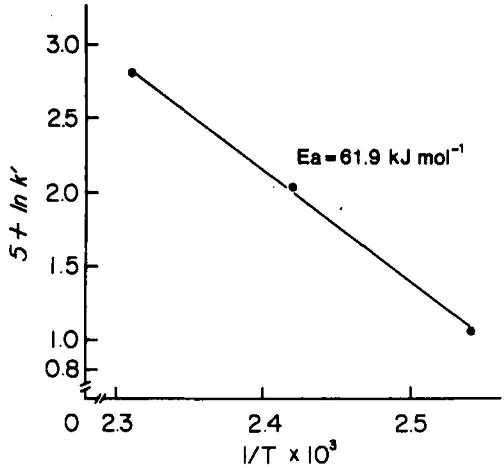


FIGURE 11. Arrhenius plot for the stabilization of hydrocellulose.

obtained. When the observed rate constants were plotted against the H_2S-concentration computed from the vapor-liquid equilibrium data for H_2S,[15] the predicted sigmoidal relation between the rate and H_2S-concentration was confirmed, as shown in Figure 9.

The actual validity of Equation (4) was further reinforced by testing whether or not a linear relationship existed between k^{-1} and $[H_2S]^{-2}$, as indicated by Equation (8). Confirmation of this expectation is clearly illustrated by Figure 10. By extrapolating the k^{-1} to $[H_2S]^{-2} = 0$, the inverse of k' can be obtained for the three temperatures studied. Figure 11 presents the Arrhenius plot for the k' values obtained. From this plot, the activation energy 61.9 kJ mol^{-1} was obtained for the stabilization reaction.

The results from the present study thus confirm the reaction mechanism proposed by Procter.[4] The stabilization reaction has an activation energy of 61.9 kJ mol^{-1} which corresponds to a 60% rate increase every 10°C rise in the temperature range of 120° to 160°C.

ACKNOWLEDGMENT

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