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The Conversion of Cellulose into Soluble Glucose Polymers in a Sulfur Dioxide Solution of Sulfur Trioxide

By Yoshio SAKAI

Faculty of Agriculture, Tokyo University of Education, Komaba, Meguro-ku, Tokyo

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The conversion of cellulose into soluble glucose polymers was shown to be composed of a set of irreversible reactions in series: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where A is cellulose; B, a soluble glucose polymer, and C, the decomposition product, which does not give reducing sugar under further hydrolysis by dilute acid. The first-order rate constants, k_1 (hr^{-1}) and k_2 (hr^{-1}), were given in 0.32 to 3.3% sulfur dioxide solutions of sulfur trioxide:

$$k_1 = 2.64 \times 10^{11} C^{1.63} \exp[-16700/(\boldsymbol{R}T)] \quad (\text{for } 0\text{—}50^\circ\text{C}),$$

and

$$k_2 = 8.99 \times 10^{15} C^{1.63} \exp[-24500/(\boldsymbol{R}T)] \quad (\text{for } 25\text{—}50^\circ\text{C}).$$

From k_1 and k_2, the sulfur trioxide concentration, C, and temperature, T, the maximum yields of the soluble glucose polymer and the time required to attain a maximum yield were obtained. It was shown that the application of the technique to wood saccharification is possible.

In a sulfur dioxide solution of sulfur trioxide, cellulose reacts with sulfur trioxide to form water-soluble cellulose sulfate.¹⁾ The product and the cellulose residue are insoluble in the solution. This is interesting from the viewpoint of wood saccharification. After the treatment of wood in a liquid sulfur dioxide solution of sulfur trioxide, the insoluble product can be easily separated from the solution. The product is water-soluble and ready for hydrolysis in a dilute acid. The recovered sulfur dioxide solution, fortified by sulfur trioxide, is readily adaptable for repeated use. If this reaction takes the place of the mainhydrolysis in wood saccharification, it is possible to regard it as a new process which can be carried out with a minimum consumption of sulfuric acid.

Materials and Methods

Materials.—*Cellulose.*—Filter paper (Tôyô Roshi, No. 2) ground to small flakes with a grater was used.

Wood.—Sawdust of Yachidamo wood (*Fraxinus mandshurica,* Rupr.) passed through a 20-mesh sieve was used. Before use the sawdust was prehydrolyzed in 10% sulfuric acid at 100°C for 3 hr., washed with water, and dried at 105°C. The prehydrolyzed wood contained 69.9% potential reducing sugar, 1.7% potential pentose, and 32.4% lignin.

Sulfur Trioxide.—An asbestos-like sulfur trioxide was redistilled before use.

Sulfur Dioxide.—Liquid sulfur dioxide distilled from the gas cylinder was used.

Procedure.—The pressure glass vessels²⁾ were used. The bottle containing a cellulose and sulfur dioxide solution of sulfur trioxide was shaken in a water-bath at different temperatures for various periods. After the reaction, the product was filtered off and the residue was washed five times with sulfur dioxide. The sulfur dioxide adsorbed on the washed product was stripped off overnight by suction. The water-insoluble part was then centrifuged and washed with water. The reducing sugar and the potential reducing sugar in the soluble and the insoluble parts were determined. The soluble part was easy to hydrolyze in dilute acid. The insoluble part was, however, as difficult to as cellulose.

Analytical Methods.—The reducing sugar was determined by Somogyi's new reagent.³⁾

The potential reducing sugar in the insoluble part was determined by the method of Saeman, Bubl and Harris.⁴⁾ From the result, the amount of unreacted cellulose was obtained.

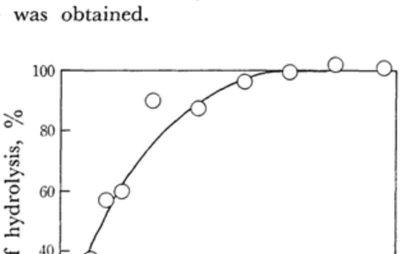

Fig. 1. Hydrolysis of soluble glucose polymer obtained in SO_2 solution of SO_3, in 2.5% HCl at 100°C.

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1) R. Asami and N. Tokura, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **62**, 1953 (1959).

2) M. Amagasa and H. Yamaguchi, *Tohoku Daigaku Hisuiyoeki Kagaku Kenkyusho Hokoku* (*Bull. Chem. Research Inst. Non-Aqueous* Soln., *Tohoku Univ.*), **1**, 181 (1951); **2**, 75, 179 (1952).

3) M. Somogyi, *J. Biol. Chem.*, **160**, 16 (1945).

4) J. F. Saeman, J. L. Bubl and E. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **17**, 35 (1945).

The determination of the potential reducing sugar in the soluble part was carried out by Somogyi's method after hydrolysis in 2.5% hydrochloric acid at 100°C for 3 hr. (Fig. 1). From the result, the amount of the soluble glucose polymer was obtained.

In this paper, the soluble glucose polymer and the unreacted and initial celluloses are expressed in terms of the potential reducing sugar.

Results and Discussion

Reaction Mechanism.—After treating cellulose in a liquid sulfur dioxide solution of sulfur trioxide for different times at 0, 25 and 50°C, the unreacted cellulose was determined. The extent of cellulose degradation was indicated by the ratio of the residual cellulose to the initial cellulose (Fig. 2). Figure 2 shows the progress of the reaction according to the equation of the first-order reaction, with reference to cellulose degradation. At the same time, the produced soluble glucose polymer was also determined as is shown in Fig. 3. The soluble glucose polymer rose to a maximum and then fell. The amount of decomposition product (the difference between the initial cellulose and the sum of the soluble and insoluble glucose polymers) rose continuously (Fig. 3). These findings suggest that the reaction belongs to a set of irreversible reactions in series:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (1)$$

where A is cellulose; B, the soluble glucose polymer; C, the decomposition product which does not give reducing sugar under further hydrolysis by dilute acid; k_1, the first-order rate constant which governs the A→B reaction, and k_2, the constant for B→C. The amounts of A and B at any time, t, are given for such a system by:

$$c_A = a\exp(-k_1t) \qquad (2)$$

$$c_B = ak_1[\exp(-k_1t)-\exp(-k_2t)]/(k_2-k_1) \qquad (3)$$

where a is the initial amount of cellulose and c_A and c_B are the amounts of A and B at time t. Equation 2 fits in with the present data, as has been described above (Fig. 2). The values of k_1 found at 30°C in a 2.2% sulfur trioxide concentration and at 50°C in a 1.1% concentration were 0.375 and 1.88 hr^{-1}. Using these k_1 values, the reaction times, t, and the corresponding amounts of the soluble glucose polymer produced, c_B, k_2 can be calculated according to Eq. 3 to be 0.0327 hr^{-1} at 30°C in 1.1% sulfur trioxide and 0.335 hr^{-1} at 50°C in 2.2% sulfur trioxide. The c_B-time curves calculated from k_1 and k_2 agreed with the observed data, as is shown in Fig. 3. These facts prove that, with reference to cellulose, the present reaction progresses according to the mechanism described by the successive first-order reactions 1.

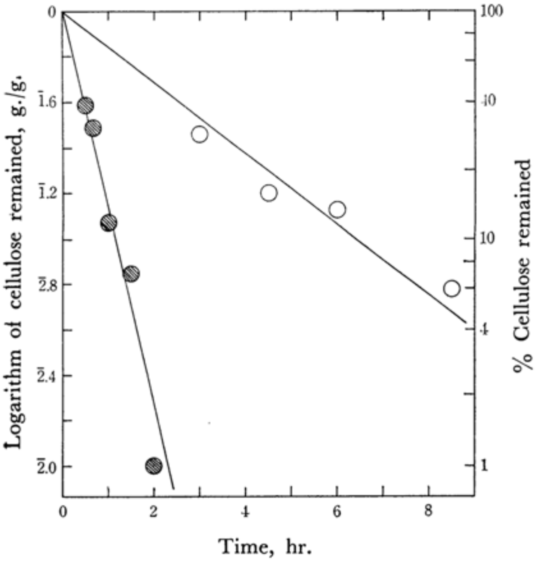


Fig. 2. Rates of cellulose degradation in SO_2 solution of SO_3.
● 50°C, SO_3 concn.: 1.1%, SO_3/cellulose: 1.1
○ 25°C, SO_3 concn.: 2.2%, SO_3/cellulose: 1.5

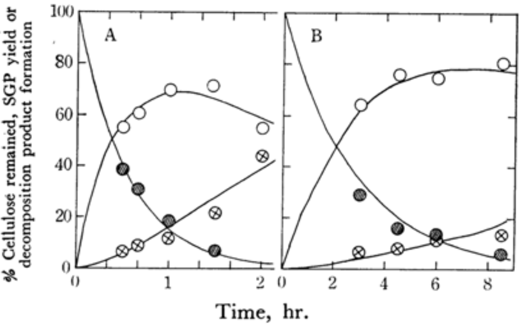


Fig. 3. Cellulose degradation to soluble glucose polymer (SGP) and simultaneous decomposition of SGP.
A 50°C, SO_3 concn.: 1.1%, SO_3/cellulose: 1.1
B 25°C, SO_3 concn.: 2.2%, SO_3/cellulose: 1.5
● Cellulose remained, g. PRS/100 g. cellulose
○ SGP yield, g. PRS/100 g. cellulose
⊗ Decomposition product formation, g. loss of PRS/100 g. of cellulose

The Rate Constant of Cellulose Degradation.—Because it was previously found that the degradation of cellulose took place as a first-order reaction, the rate constants, k_1, were determined, using Eq. 2 and the c_A/a values observed in sulfur trioxide concentrations ranging from 0.32 to 3.3% at 0, 25, and 50°C for various times. The k_1's (hr^{-1}) are shown in Table I. When the logarithm of the reaction rate constant was plotted against the logarithm of the percentage concentration of sulfur trioxide in a liquid sulfur dioxide solution, the parallel straight lines were obtained at intervals depending on the temperature (Fig. 4). The slope of the lines is 1.63. The plotting of the logarithm of k_1 at a 1% sulfur trioxide concentration (Fig. 4) against the reciprocal of the absolute temperature

TABLE I. FIRST-ORDER REACTION RATE CONSTANTS OF CELLULOSE DEGRADATION (k_1) AND SOLUBLE GLUCOSE POLYMER DESTRUCTION (k_2)

Temp. °C	SO_3 concn. %	$\frac{SO_3}{\text{cellulose}}$ g./g.	k_1 Obsd. hr^{-1}	k_1 Calcd. hr^{-1}	k_2 Obsd. hr^{-1}	k_2 Calcd. hr^{-1}
0	0.44	0.17	0.00281	0.00304		
	0.60	0.17	0.00674	0.00502		
	1.22	0.55	0.0345	0.0159		
	1.90	0.84	0.0272	0.0329		
	2.07	1.11	0.0672	0.0378		
	2.50	0.71	0.0341	0.0515		
25	0.32	0.64	0.0762	0.0225	0.00173	0.00161
	0.50	0.49	0.0400	0.0466	0.00394	0.00334
	0.50	1.10	0.124	0.0466	0.00491	0.00334
	0.93	1.00	0.102	0.128	0.00695	0.00917
	2.20	1.50	0.412	0.521	0.0550	0.0373
	2.20	1.50	0.403	0.521	0.0348	0.0373
	2.20	1.50	0.333	0.521	0.0373	0.0373
	2.20	1.50	0.332	0.521	0.0260	0.0373
	2.96	1.87	0.768	0.844	0.0250	0.0578
	3.30	2.26	1.00	1.01		
50	0.45	0.80	0.810	0.347	0.0508	0.0593
	0.48	0.49	0.439	0.388	0.0275	0.0661
	0.91	0.53	0.487	1.10	0.128	0.188
	0.92	0.53	0.532	1.12	0.203	0.191
	0.97	1.42	1.42	1.22	0.435	0.208
	1.05	1.10	1.88	1.39	0.388	0.237
	1.05	1.10	1.76	1.39	0.351	0.237
	1.05	1.10	2.24	1.39	0.360	0.237
	1.05	1.10	1.72	1.39	0.243	0.237
	1.05	1.10	2.30	1.39	0.237	0.237
	1.20	1.64	1.82	1.72	0.487	0.293
	1.28	0.63	1.16	1.94		

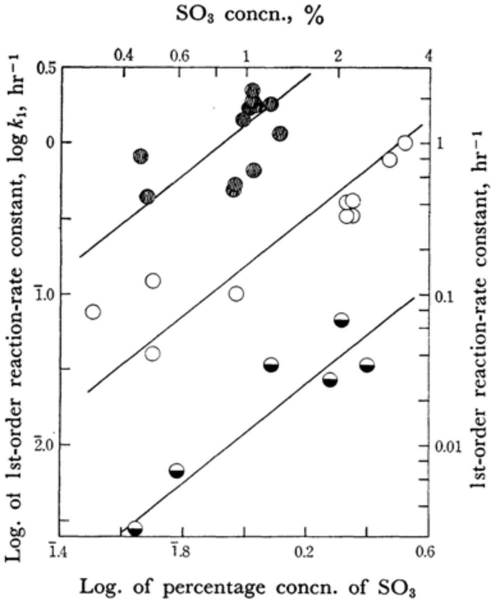


Fig. 4. First-order reaction-rate constants of cellulose degradation in various concentrations of SO_2 solution of SO_3 at 0, 25, and 50°C.
▨ 50°C, ○ 25°C, ◒ 0°C

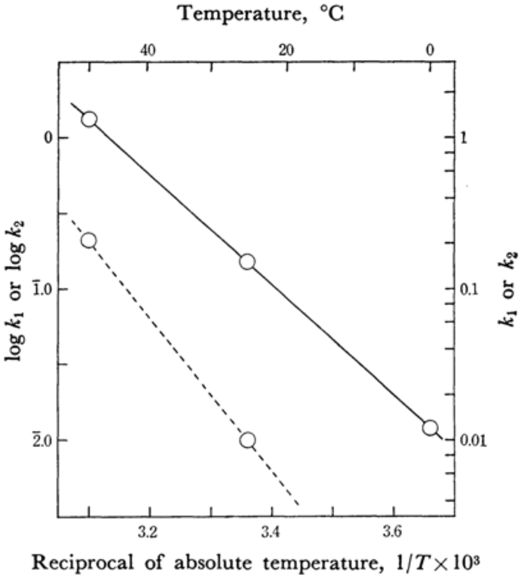


Fig. 5. First-order reaction-rate constants of celulose degradation (——) and soluble glucose polymer decomposition (----) in 1% SO_2 solution of SO_3 at different temperatures.

gives the straight line shown in Fig. 5. The slope of the line is −3650°K. Using these two values, the following experimental equation, which fits the observed k_1 (hr^{-1}) values (Table I), was obtained:

$$\log k_1 = 11.4215 + 1.63 \log C - 3650(1/T)$$

$$\text{or} \quad k_1 = 2.64\times 10^{11}\, C^{1.63} \exp[-16700/(\mathbf{R}T)] \qquad (4)$$

where C is the sulfur trioxide concentration in liquid sulfur dioxide; T, the absolute temperature (273—323°K), and $\boldsymbol{R}$, the gas constant (cal./deg.).

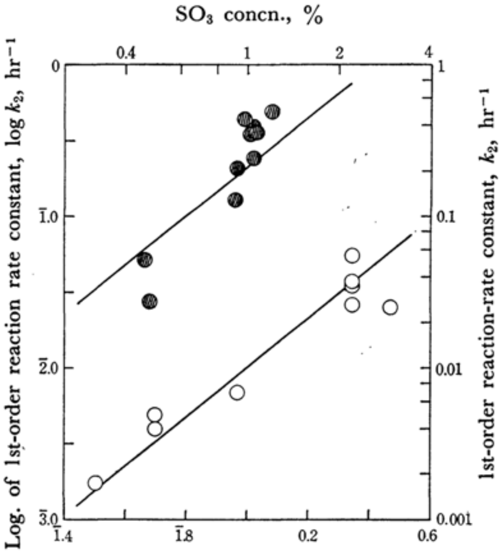


Fig. 6. First-order reaction-rate constants of soluble glucose polymer decomposition in various concentrations of SO_2 solution of SO_3 at 25 and 50°C.
● 50°C, ○ 25°C

The Rate Constant of the Decomposition of the Soluble Glucose Polymer to Substances Other than Reducing Sugar.—The soluble glucose polymer yield, c_B, at the time t and the corresponding k_1 (hr^{-1}) value gave the k_2 (hr^{-1}) value according to Eq. 3. The values are shown in Table I. The values at 0°C were so small that they could be taken as zero. The equation describing k_2 (hr^{-1}) as a function of the temperature and of the sulfur trioxide concentration was obtained in the same manner as the equation describing k_1 (Figs. 5 and 6):

$$\log k_2 = 15.953 + 1.63 \log C - 5380(1/T)$$

$$\text{or} \quad k_2 = 8.99\times 10^{15}\, C^{1.63} \exp[-24600/(\mathbf{R}T)] \qquad (5)$$

Maximum Yield.—The yield of the soluble glucose polymer at the maximum is given by:

$$c_B = K^{1/(1-K)}$$

$$\text{where} \quad K = k_1/k_2 = 2.94\times 10^{-5} \exp(3990/T) \qquad (6)$$

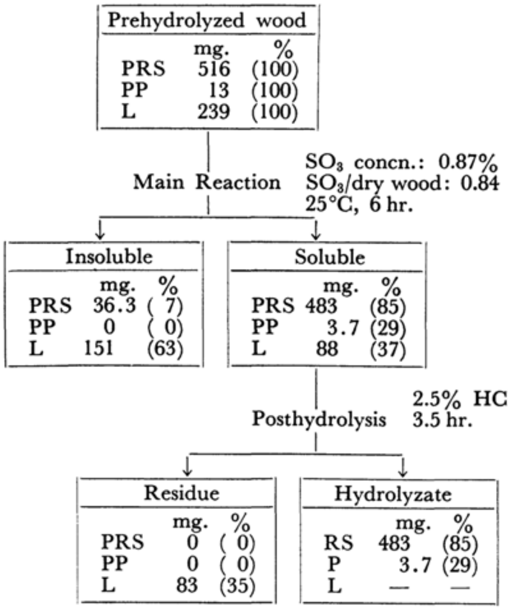
For example, the maximum yields are 84 and 72% at 25 and 50°C. At a lower temperature, such as 0°C, the yield must be higher than that given by the equation, because scarcely any sugar decomposition occured.

The yield of the soluble glucose polymer reaches a maximum at the time, t_m (hr.), given by Eq. 7.

$$t_m = 2.303(\log k_1 - \log k_2)/(k_1 - k_2) \qquad (7)$$

where k_1 and k_2 are given by Eqs. 4 and 5. For example, a reaction time of 1.7 hr. is necessary to obtain the maximum yield at 50°C, and 6.6 hr, at 25°C.

Application to Wood Saccharification.—The prehydrolyzed sawdust of hardwood was treated by a sulfur dioxide solution of sulfur trioxide. The results are shown in Fig. 7. Although a portion of lignin was dissolved in the solution, it precipitated again after the dilute acid hydrolysis.



Prehydrolyzed wood	mg.	%
PRS	516	(100)
PP	13	(100)
L	239	(100)

Insoluble	mg.	%
PRS	36.3	(7)
PP	0	(0)
L	151	(63)

Soluble	mg.	%
PRS	483	(85)
PP	3.7	(29)
L	88	(37)

Residue	mg.	%
PRS	0	(0)
PP	0	(0)
L	83	(35)

Hydrolyzate	mg.	%
RS	483	(85)
P	3.7	(29)
L	—	—

Fig. 7. Saccharification of prehydrolyzed hardwood using sulfur dioxide solution of sulfur trioxide.
PRS: potential reducing sugar, RS: reducing sugar, PP: potential pentose, P: pentose, L: lignin

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