

Oxidation of Cellulose by Ceric Ion

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Synopsis

Dissolving pulp was oxidized by ceric ammonium sulfate in sulfuric acid medium under oxygen-free argon. Initial rapid oxidation was followed by first-order consumption of ceric ion. The rate of cellulose oxidation ($-R_{Ce}$) which was taken at the beginning of the first order consumption period, levelled off with an increase in the concentration of ceric ion. It was found that the $-R_{Ce}$ was dependent on the concentration of cellulose in the second power. The rate of ceric ion consumption was a function of the available surface area of cellulose.

INTRODUCTION

The mechanism of oxidation of alcohols by ceric ion has been studied in a number of publications. The oxidation of alcohols, as applied to the initiation of grafting onto cellulose, has been recently reviewed by McDowall et al.¹ The mechanism of oxidation is dependent on the type of ceric salt and reaction medium used. Oxidation of alcohols occurs through the formation of a complex in perchloric and nitric acids, while in sulfuric acid the oxidation is a direct-bimolecular reaction of the second order.

Cellulose is an insoluble and mostly crystalline substance, as the result of which it is very difficult to study the oxidation-reaction of such material. Several papers²⁻⁹ have been published on the oxidation of cellulosic materials by ceric salts but the results presented have been qualitative only. Furthermore, the experiments described were carried out in the presence of air or sometimes under nitrogen but without any guarantee of the complete removal of oxygen. It has been recently reported by Graczyk and Hornof¹⁰ that oxidation of cellulose is higher in the presence of air than under oxygen-free argon.

Quantitative results presented so far have been limited only to glucose and its derivatives as a model reaction for cellulose. Most studies emphasized the localization of the oxidative sites on cellulose. Kulkarni and Mehta⁴ found that the model compounds containing a hemiacetal unit as glucose were more readily oxidized than compounds in which these groups are blocked, such as α -methylglucose. Hintz and Johnson¹¹ studied model compounds and found that oxidation of cellulose with ceric ion occurs mainly at the C_2-C_3 glycol group and not the C_6 position. Pottenger and Johnson,³ on the basis of oxidation of model compounds for cellulose, also found that the rate of oxidation of hemiacetal units was 360 times that of C_2-C_3 bonds compared

with the number of end groups, allowing them to become probable reaction sites.

The ceric method is often used to initiate grafting of vinyl monomers onto cellulose. Although considerable effort has been made to explain the mechanism of grafting by ceric ion, details are still unknown, e.g., the kinetics of cellulose oxidation. The purpose of this paper is to study the mechanism of oxidation of cellulose by ceric ammonium sulfate in sulfuric acid medium under oxygen-free argon.

EXPERIMENTAL

Material

A never dried dissolving pulp (supplied by Zakłady Celulozy i Papieru in Swiecie, Poland) was washed four times in 2L of distilled water and then drained. The resulting pulp, containing 80% moisture, was kept in a freezer. Ceric ammonium sulfate (BDH) was reagent grade.

Oxidation

The reaction was carried out in a 1-L reactor as described previously.¹² In a typical experiment the reactor was charged with 4.5 g (dry weight) pulp, 15.3 mL 6N H₂SO₄, and a suitable amount of double distilled water to adjust the volume to 450 mL. The concentration of sulfuric acid in the reaction medium was 1%. After 2 h of purging the reactor with oxygen-free argon, the reaction of oxidation was started by the immersion of a small cup with the desired amount of ceric salt into the reaction mixture. The cup was washed and immediately raised back above the liquid surface by a wire attached to the cup. This method of adding ceric salt prevented any traces of oxygen from entering the reactor.

Determination of Ceric Ion

Ceric ion was determined by the standard procedure described elsewhere.¹²

RESULTS AND DISCUSSION

Effect of Ceric Ion Concentration

The typical curve of Ce⁺⁴ consumption as a function of time is shown in Figure 1. There are three specific regions on the curves. The initial rapid Ce⁺⁴ consumption reaction is followed by a slow one. When consumption of Ce⁺⁴ exceeds 70–80%, the rate of oxidation accelerates again. The size of each of these regions is dependent upon the relative concentration of ceric ion to cellulose concentration and the temperature of the reaction. Different concentrations of ceric ion are shown in Figure 2. A 1-h initial rapid reaction is followed by the first-order dependence. However, the slope of semilogarithmic plots decreases with an increase in the concentrations of ceric ion. This trend is better seen in Figure 3, where the rate of oxidation ($-R_{Ce}$) was determined at the beginning of the first-order consumption period and plotted against the concentration of ceric ion. The increments in the rate of ceric consumption

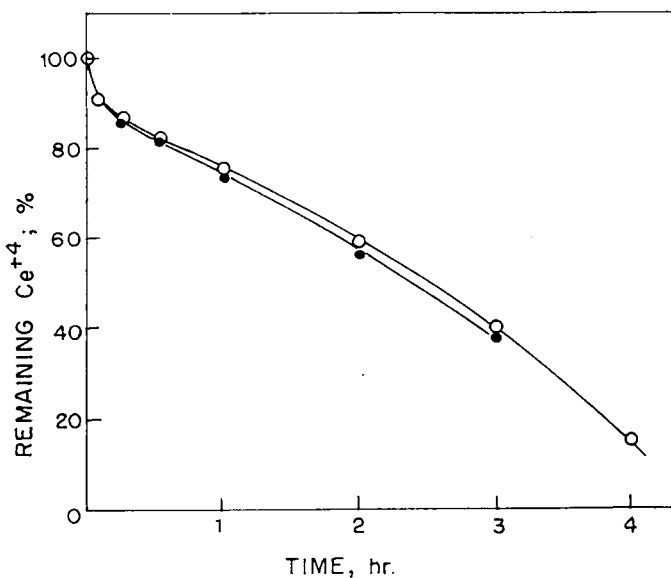


Fig. 1. Consumption of Ce^{+4} as a function of time and stirring speed: temperature = 45°C; [cellulose] = 10 g/L; [Ce^{+4}] = 2.5 mmol/L; (○) 60 rpm; (●) 810 rpm.

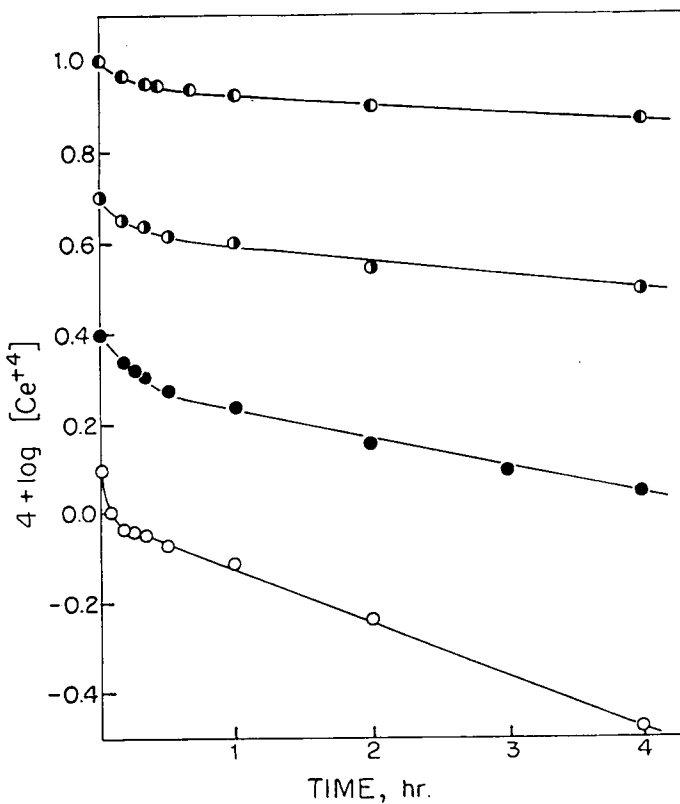


Fig. 2. Dependence of Ce^{+4} consumption on time: temperature = 25°C; [cellulose] = 10 g/L; [Ce^{+4}]: (○) 0.125 mmol/L; (●) 0.25 mmol/L; (◐) 0.5 mmol/L; (◑) 1 mmol/L.

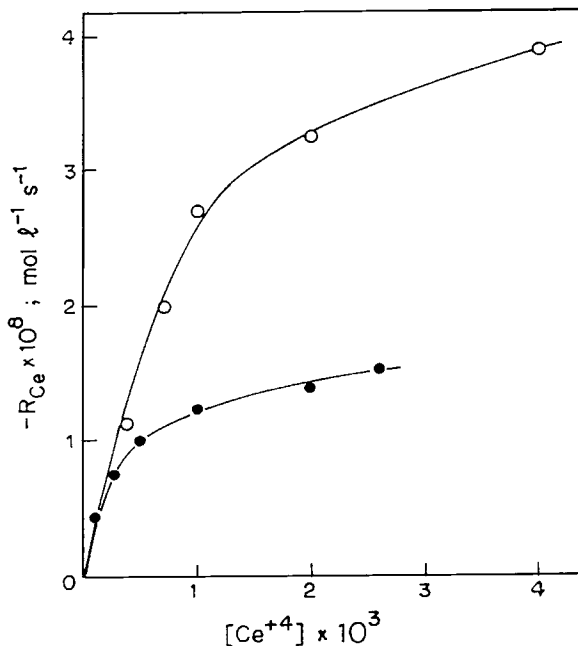


Fig. 3. Rate of Ce^{+4} consumption as a function of Ce^{+4} concentration: [cellulose] = 10 g/L; (○) 45°C; (●) 25°C.

decrease with an increase in ceric ion concentration and probably levels off at a higher ion concentration.

The experimental data can be explained by the fact that the dissolving pulp used in the work was mostly crystalline cellulose with approximately 20% amorphous region. The oxidation of cellulose takes place in the amorphous region and on the surface of the oriented regions (crystallites) in the fibers. As a result, the phenomenon of saturation of cellulose by ceric ion with an increase in ceric ion concentration is observed.

Effect of Cellulose Concentration

Plot $d \log[\text{Ce}^{+4}]/dt$ vs. cellulose concentration is shown in Figure 4. Excellent correlation is obtained when the concentration of cellulose is in the second power.

The set of experiments in which the rate of alcohol oxidation by ceric ion is studied as a function of alcohol concentration is a useful method for the determination of the mechanism of the oxidation. When the rate of oxidation reaction levels off with an increase in the concentration of alcohol, it means that a complex is formed between alcohol and ceric ion. On the other hand, first-order dependence indicates that oxidation is a direct bimolecular reaction.

Oxidation of cellulose as a mostly crystalline substrate is dependent on surface available. The importance of surface area in enzymatic cellulose hydrolysis is reported in several works.¹³⁻¹⁵ King¹⁶ found that the rate of enzymatic degradation of the crystalline hydrocellulose was a linear function

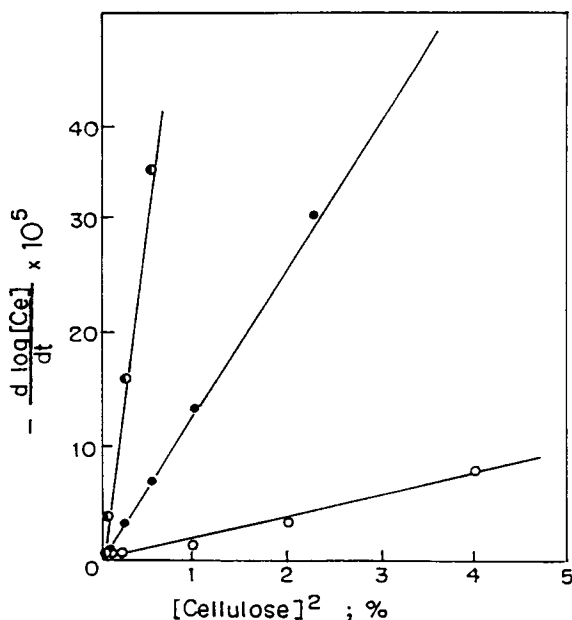


Fig. 4. Rate of Ce^{+4} consumption (k) as a function of cellulose concentration: $[\text{cellulose}] = 10$ g/L; $[\text{Ce}^{+4}] = 0.25$ mmol/L; (○) 25°C; (●) 45°C; (●) 65°C.

of the surface area available in the second power. Thus, assuming that the concentration of cellulose is directly proportional to the surface area, the concentration of cellulose in the second power is obtained. In other words, if the surface area phenomenon is eliminated, the reaction becomes first-order-dependent on cellulose. This means that the oxidation of cellulose is a direct reaction without the creation of a complex as has been well established in the case of the oxidation of alcohols in sulfuric acid medium.

Effect of Agitation

Bayat-Makeoi and Goldstein¹⁷ found that hydrolysis of cellulose with hydrochloric acid enhanced by cations was strongly dependent on the degree of agitation. On the plot $\log [\text{cellulose}]$ remaining vs. time, two straight lines were observed. The initial rate of hydrolysis is very fast and nearly independent of the agitation. In the second phase, the rate of hydrolysis increases with an increase in the number of oscillations. The two-phase course of the hydrolysis is most apparent without agitation, and changes completely to a single phase under rapid shaking.

The reaction of cellulose oxidation is a heterogeneous one. The adsorption of ceric ion and the oxidation of cellulose occurs in the amorphous phase and on the surface of the crystalline phase. Since the dissolving pulp was mostly crystalline cellulose (80%) and the rate of cellulose oxidation is limited to the available surface, the applied agitation should have some effect.

Tables I and II show the effect of agitation on cellulose oxidation at different concentrations of cellulose and ceric ion. For comparison, the data for oxidation of cellulose in the presence of nitrogen 99.9% are presented in

TABLE I
Effect of Agitation on the Amount of Remaining Ceric Ion^a

rpm	Remaining Ce ⁺⁴ (%)		rpm
	[Ce ⁺⁴] = 0.5 mmol/L	[Ce ⁺⁴] = 2.5 mmol/L	
60	50.5	82.7	60
160	51.3	82.6	210
510	52.0	83.0	710
810	51.9	82.1	810

^a Reaction conditions: temp = 35°C; reaction time = 0.5 h; [cellulose] = 20 g/L.

TABLE II
Effect of Agitation on the Amount of Remaining Ceric Ion^a

rpm	Remaining Ce ⁺⁴ (%)		
	Argon	Nitrogen (99.9%)	
60	51.3; 52.5		42.2
310	42.4; 43.0		46.6
1000	43.3; 44.4		41.7

^a Reaction conditions: temp = 45°C; [cellulose] = 10 g/L; [Ce⁺⁴] = 1 mmol/L; reaction time = 0.5 h.

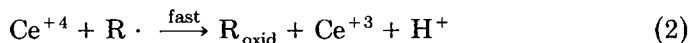
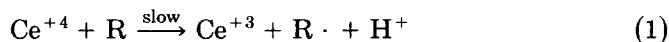
Table II. At a cellulose concentration of 20 g/L with a Teflon paddle stirrer, no effect of agitation is observed. However, at a lower cellulose concentration (10 g/L) there is a slight effect of agitation. Under oxygen-free argon, the amount of remaining Ce⁺⁴ is a little higher at a low stirring speed in comparison to the two other agitation speeds.

The very small dependence of Ce⁺⁴ consumption on agitation even at very low concentration of cellulose (10 g/L) is probably caused by the low energy of mixing by the Teflon propeller. The energy of mixing is insufficient to disintegrate the oriented regions (crystallites) in the fibers and to increase the surface area. Consequently, very slight or no effect of agitation is observed.

Figure 1 shows the consumption of ceric ion as a function of time for two different stirring speeds. There is a small difference between low and high stirring speeds.

Oxidation Mechanism and Rate Law

The following mechanism is proposed to explain the experimental results:



where R is cellulose.

The oxidation of cellulose is a direct reaction without creation of complex as was generally accepted for the reaction in sulfuric acid medium. Creation of radicals on cellulose is a slow reaction which is followed by a fast reaction of

TABLE III
Rate of Cellulose Oxidation in Different Temperatures^a

Temperature (°C)	$k \times 10^7$ (L/g s)
25	0.52
45	3.55
65	15.5

^a Reaction conditions: [cellulose] = 10 g/L; [Ce⁺⁴] = 0.25 mmol/L.

oxidation by the second molecule of ceric ion. The rate of consumption of ceric ion can be expressed by

$$-R_{\text{Ce}} = k[\text{Ce}^{+4}][\text{cellulose}]^2 \quad (3)$$

when [cellulose] \gg [Ce⁺⁴] the equation has the form

$$-R_{\text{Ce}} = k'[\text{Ce}^{+4}] \quad (4)$$

where $k' = k[\text{cellulose}]^2$.

At a constant concentration of cellulose, the rate of the reaction is first order with respect to the concentration of total ceric ion with the exception of initial and final rate of reaction and can be presented by

$$-d[\text{Ce}^{+4}]/dt = k'[\text{Ce}^{+4}] \quad (5)$$

The values of k' were calculated from the slope of the plots $\log[\text{Ce}^{+4}]$ vs. time. From the slope of the plots k' vs. cellulose concentration in the second power the values of the third-order constant (k) were calculated. The values of k for three different temperatures are presented in Table III.

The activation energy of the reaction of cellulose oxidation by ceric ammonium sulfate in sulfuric acid medium was found to be 18.1 kcal/mol. This value is in the same range as activation energy of oxidation of alcohols in sulfuric acid medium.¹⁸

Results presented above led to the conclusion that cellulose oxidation is a bimolecular reaction in sulfuric acid medium and the rate of oxidation is dependent on cellulose concentration in the second power.

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