

## ESR Study of Reactions of Cellulose with $\cdot\text{OH}$ Generated by $\text{Fe}^{+2}/\text{H}_2\text{O}_2$

JETT C. ARTHUR, JR., OSCAR HINOJOSA, and M. S. BAINS,  
*Southern Regional Research Laboratory, Southern Utilization Research  
and Development Division, Agricultural Research Service,  
U. S. Department of Agriculture, New Orleans, Louisiana 70119*

### Synopsis

It was demonstrated by ESR spectroscopy that the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system gave a reactive species which generated an ESR triplet spectrum or sorbitol similar to that generated by hydroxyl radicals from the  $\text{Ti}^{+3}/\text{H}_2\text{O}_2$  system. An ESR spectrum was obtained for the hydroxyl radicals generated by the latter system. However, the lifetime of hydroxyl radicals, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, was apparently very short, and an ESR spectrum for the hydroxyl radicals, generated by this system, was not observed. The  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system also generated triplet spectra with cotton cellulose I, cotton cellulose II, and microcrystalline cellulose, suggesting that a hydrogen atom had been abstracted from the hydroxyl group on carbon  $\text{C}_6$ , or possibly the hydrogen atom on carbon  $\text{C}_5$ . The ESR spectrum generated on microcrystalline cellulose was less intense than those generated on cellulose I and II. On initiation of graft polymerization of the activated celluloses with acrylonitrile, the triplet spectrum disappeared and was replaced by two strong singlet spectra. One of the singlet spectra was likely generated on carbon  $\text{C}_1$  or  $\text{C}_4$  on depolymerization of the cellulose molecule, and the other was probably generated on the end of the growing polyacrylonitrile molecular chain. The absence of a triplet spectrum gave direct evidence for the order in which the acrylonitrile monomer was being grafted onto the cellulose molecule. The mechanisms proposed by Haber and Weiss for the reactions generated in the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system were generally supported.

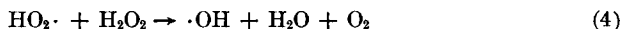
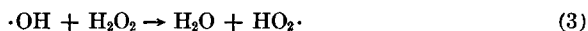
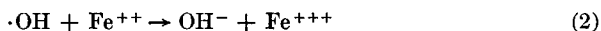
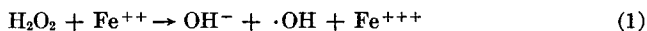
### INTRODUCTION

The ESR investigations of free radical-initiated reactions of fibrous cotton cellulose, in which the initial free radical was formed on the cellulose molecule, have been previously reported. The formation of free radicals on the cellulose molecule through the interaction of light, high-energy radiation, or heat with cellulose and through the ceric-cerous redox reaction with cellulose has been demonstrated.<sup>1-8</sup> Graft copolymerization reactions of vinyl monomers with cellulose, initiated at the free-radical sites formed on the cellulose molecule by interaction with high-energy radiation<sup>9</sup> or with ceric ion<sup>8</sup> have also been followed by ESR spectroscopy. Other graft copolymerization reactions initiated by light or heat have been reported to be free-radical processes.<sup>10</sup>

The interaction of light<sup>1,2</sup> or high-energy radiation<sup>5,6</sup> with cellulose and the localization of the absorbed energy caused homolytic reactions, leading

to dehydrogenation, dehydroxylation, or cellulosic chain cleavage. On the initiation of these reactions, free radicals were formed on the cellulose molecule. In the redox system, ceric ion interacted with the cellulose molecule, probably at the hydroxyl groups on carbons C<sub>2</sub> and C<sub>3</sub> which resulted in the transfer of electrons from the hydroxyl groups to the ceric ion and formation of free radicals on the cellulose molecule.<sup>8</sup> In the case of thermal initiation, cellulosic chain cleavage occurred, and free radicals were formed at the location of the chain scissions.<sup>7</sup> When vinyl monomers were reacted at these activated sites, graft copolymerization reactions occurred.<sup>8,9</sup>

Graft copolymerization reactions of vinyl monomers with fibrous cotton cellulose and regenerated fibrous cellulose have previously been carried out by generating hydroxyl radicals which abstract hydrogen atoms from the cellulose molecule. Generally, the ferrous ion/hydrogen peroxide reaction to form hydroxyl radicals, reported by Haber and Weiss in 1932, is used.<sup>11-13</sup> Their proposed reaction mechanism was as shown in eqs. (1)-(4)



Merz and Waters suggested the use of hydroxyl radicals formed in the Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub> reaction to abstract hydrogen from cellulose in the presence of vinyl monomers.<sup>14</sup> Landells and Whewell reported the graft copolymerization of several vinyl monomers with regenerated fibrous cellulose by using Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub> in solutions of either acetic or sulfuric acid.<sup>15,16</sup> Richards investigated the use of Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub> for initiating graft copolymerization reaction of styrene and acrylonitrile with cotton and fibrous cellulose triacetate.<sup>17</sup> He reported more reaction with cellulose triacetate than with cotton and attributed this to the greater base exchange capacity of the cellulose triacetate. Bridgeford used FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> and heat to initiate graft copolymerization of a number of vinyl monomers onto cotton, rayon, cellulosic films, and pulp; he also reported that base exchange capacity was a factor in determining the extent of reaction of monomer with a cellulosic substrate.<sup>18</sup>

Experimental data are presented in this report, based on an ESR spectroscopy study of the reactions of hydroxyl radicals generated by the Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub> system with microcrystalline cellulose and fibrous cotton cellulose and of the graft copolymerization reactions of these activated celluloses with acrylonitrile. Although hydroxyl radicals, generated by the Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub> system, were not observed directly, they were shown to abstract hydrogen atoms from sorbitol similarly to hydroxyl radicals generated by the Ti<sup>+3</sup>/H<sub>2</sub>O<sub>2</sub> system which could be observed directly.

## EXPERIMENTAL

### Preparation of Samples

Cotton cellulose of the Deltapine variety was purified by extraction with hot ethanol; then, while the cellulose was kept immersed in dilute sodium hydroxide solution, the solution was brought to a boil. The cotton was washed with distilled water to free the cellulose of sodium hydroxide, then soured with dilute acetic acid, and later neutralized with dilute ammonium hydroxide solution. Finally, the cotton was washed with distilled water and air-dried at room temperature. The cotton was conditioned at 21°C. and 65% R.H. The purified cotton cellulose with lattice type I had a moisture content of about 7% and a viscosity-average molecular weight of about 700,000.<sup>19</sup>

To obtain cellulose with lattice type II, samples of the purified cotton cellulose were immersed in 23% sodium hydroxide solution at 25°C. for 10 min., then washed with distilled water to remove the alkali, and air-dried at room temperature.

The microcrystalline cellulose, obtained from a commercial source, had an average level-off degree of polymerization of about 220.<sup>20</sup> Other chemicals used were reagent grade.

### Methods

The ESR spectra and free radical concentrations formed during reactions of the hydroxyl radicals, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, with cellulose were determined in a Varian 4502-15 EPR spectrometer system. The system was equipped with a dual sample cavity, both aqueous solution and solid sample cell accessories, and a variable temperature accessory allowing operation from about  $-185$  to  $300^\circ\text{C}$ . A time-averaging computer accessory was used to increase the sensitivity of the spectrometer system; relative amplifications of the ESR signals greater than  $5000\times$  were obtained by using the computer accessory in combination with the spectrometer system.

The ESR spectra of cellobiose and sorbitol radicals generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system were observed by using an aqueous flow cell at  $25^\circ\text{C}$ . as previously described.<sup>21</sup> One reservoir was charged with  $0.01M$   $\text{FeSO}_4$ ,  $0.03M$   $\text{H}_2\text{SO}_4$ , and  $0.05M$  carbohydrate; the other reservoir was charged with  $0.03M$   $\text{H}_2\text{O}_2$ ,  $0.03M$   $\text{H}_2\text{SO}_4$ , and  $0.05M$  carbohydrate. The reactant reservoirs were pressurized with nitrogen (0.5 atm.). The flow rate of mixing of the solutions in the aqueous sample cell in the resonant cavity was determined by adjusting a clip on the exit lines.

The ESR spectra, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system with cellulose, were obtained by wetting the cellulose with  $0.1M$   $\text{FeSO}_4$  and then drying in a stream of nitrogen. A solution of  $0.3M$   $\text{H}_2\text{O}_2$  was drawn onto the cellulose; then the reactants were immediately frozen by immersing them in liquid nitrogen. The spectra were recorded after warming to the indi-

cated temperatures. Graft copolymerization reactions of acrylonitrile with cellulose were initiated by saturating the  $\text{H}_2\text{O}_2$  solution with the monomer and then drawing this solution onto the cellulose, which had been previously contacted with  $\text{FeSO}_4$  solution. The ESR spectra are photographs of experimentally recorded curves. The rate curves were calculated from peak-to-peak values of the signal strengths of ESR spectra recorded with a sweep time of 30 sec.

## RESULTS AND DISCUSSION

### Hydroxyl Radical Formation

When  $\text{TiCl}_3$  and  $\text{H}_2\text{O}_2$  were mixed in the aqueous sample cell in the resonant cavity, a narrow singlet spectrum with a line width of 1 gauss was obtained.<sup>21</sup> Dixon and Norman attributed this spectrum to the formation of a hydroxyl radical.<sup>22</sup> Considering the Haber and Weiss proposed reaction mechanism,<sup>12,13</sup> if  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  were mixed in the aqueous sample cell in the resonant cavity, it was expected that a similar spectrum would be obtained for the postulated hydroxyl radical. In flow experiments  $\text{FeSO}_4$  was varied from 0.01 to 0.1*M*;  $\text{H}_2\text{O}_2$  was varied from 0.025 to 0.15*M*;  $\text{H}_2\text{SO}_4$  was varied from 0.00 to 0.135*M*; flow rates were varied from flow-

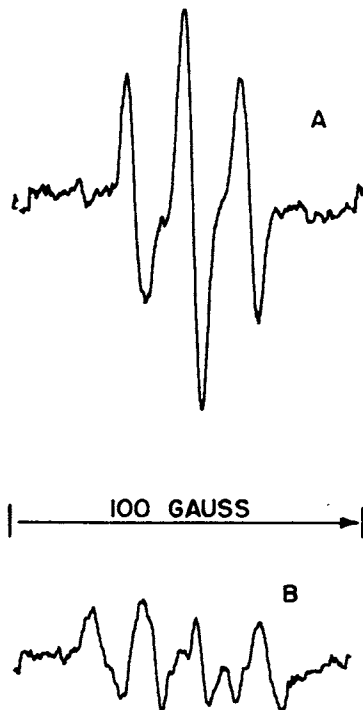


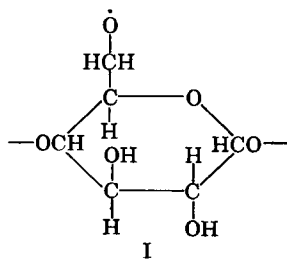
Fig. 1. ESR spectra of (A) sorbitol and (B) cellobiose generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system at 25°C. ( $\times 5000$ ).

stop-flow to 1 ml./min. to 6 ml./min. ESR spectra for the postulated hydroxyl or hydroperoxy radicals were not obtained. This suggested that the reaction mechanism step (2) proposed by Haber and Weiss<sup>12,13</sup> was very rapid, as compared with step (1).

When hydroxyl radicals, generated by the  $\text{Ti}^{+3}/\text{H}_2\text{O}_2$  system, for which an ESR spectrum was obtained, were formed in a solution of carbohydrates, hydrogen atoms were abstracted from the carbohydrate to give a characteristic ESR spectrum.<sup>21</sup> For example, the ESR spectrum of sorbitol, generated by the hydroxyl radical from the  $\text{Ti}^{+3}/\text{H}_2\text{O}_2$  system, was a triplet (1:2:1,  $\Delta H = 17.5$  gauss). In a similar flow experiment, the ESR spectrum of sorbitol, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, is shown in Figure 1A. A triplet spectrum (about 1:2:1,  $\Delta H = 15\text{--}17$  gauss) was obtained. The radical species, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, reacted with sorbitol similarly to the reaction of the hydroxyl radical, generated by the  $\text{Ti}^{+3}/\text{H}_2\text{O}_2$  system, with sorbitol. This would suggest that the hydroxyl radical generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ , proposed by Haber and Weiss,<sup>12,13</sup> likely occurred. The ESR spectrum of cellobiose generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system is shown in Figure 1B and is similar to that generated by the  $\text{Ti}^{+3}/\text{H}_2\text{O}_2$  system.

### Cotton Cellulose I

Fibrous cotton cellulose I was put into the aqueous sample cell in the resonant cavity. Solutions of 0.1M  $\text{FeSO}_4$  and 0.3M  $\text{H}_2\text{O}_2$  were mixed in the cell at 25°C. while flowing through the cellulose. A very weak and undefined ESR spectrum of cellulose was generated. In another experiment, the fibrous cellulose was immersed in 0.1M  $\text{FeSO}_4$  for at least 15 min. to wet the fiber thoroughly and then dried in a flowing stream of nitrogen. Then this dried cellulose, containing  $\text{FeSO}_4$ , was put in a quartz tube, and 0.3M  $\text{H}_2\text{O}_2$  was drawn onto the cellulose. Immediately the tube and its contents were immersed in liquid nitrogen. The ESR spectrum, which was generated, is shown in Figure 2 and was determined at  $-110^\circ\text{C}$ . The weak signal was amplified 5000  $\times$  in the spectrometer system and accumulated by sweeping sixteen times with the time averaging computer to give an amplification of about 20,000  $\times$ . The three intense lines appeared to be a triplet (about 1:2:1,  $\Delta H = 31$  gauss). This could be attributed to the radical resulting from the abstraction of the hydrogen atom from the hydroxyl group on carbon  $\text{C}_6$  (I):



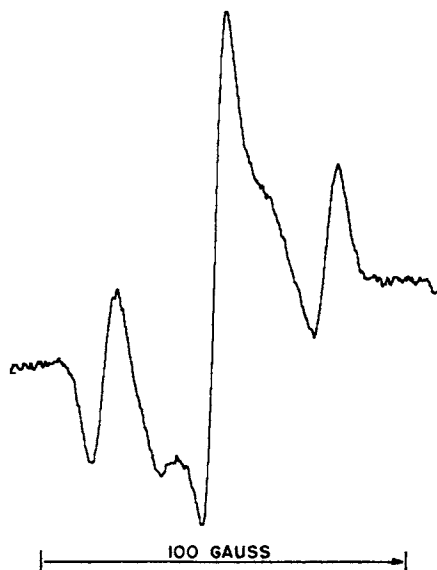


Fig. 2. ESR spectra of cotton cellulose I generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, recorded at  $-110^\circ\text{C}$ . ( $\times 20,000$ ).

The ESR spectrum generated was very sensitive to temperature; if the temperature was increased to  $-60^\circ\text{C}$ ., the spectrum became very weak and undefined within a few minutes. There is an indication of two poorly defined additional lines which could also be interpreted as a triplet in combination with the intense central line (about 1:2:1,  $\Delta H = 12$  gauss). This could indicate the presence of a second radical formed by the abstraction of the hydrogen atom from carbon  $\text{C}_5$ . The relative concentration of this radical to the one proposed on carbon  $\text{C}_6$  would be very weak.

### Copolymerization Reactions

Fibrous cotton cellulose I was immersed in  $0.1M$   $\text{FeSO}_4$  for at least 15 min. to wet the fiber thoroughly and then dried in a flowing stream of nitrogen. Then this dried cellulose containing  $\text{FeSO}_4$  was put in a quartz tube, and  $0.3M$   $\text{H}_2\text{O}_2$  saturated with acrylonitrile monomer was drawn onto the cellulose. Immediately the tube and its contents were immersed in liquid nitrogen. The ESR spectrum, which was generated, shown in Figure 3, was determined at  $-110^\circ\text{C}$ . This ESR spectrum, generated in cellulose during the copolymerization reaction, was several times more intense than the ESR spectrum, generated in cellulose by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system.

The triplet spectrum disappeared during the graft copolymerization reaction. The spectrum, shown in Figure 3, could be interpreted as two strong singlet spectra, one with  $\Delta H =$  about 15 gauss and the other with  $\Delta H =$  about 62 gauss. The narrower singlet spectrum probably resulted from depolymerization of the cellulose molecule due to the abstraction of

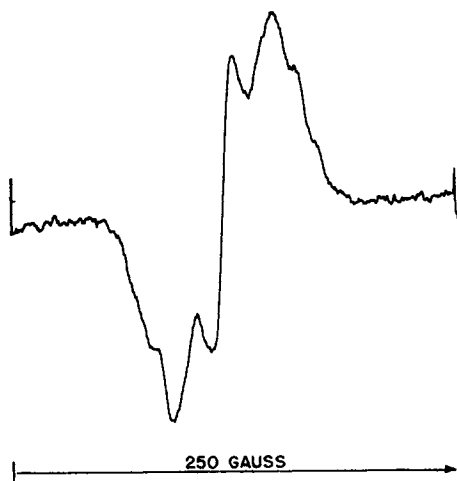
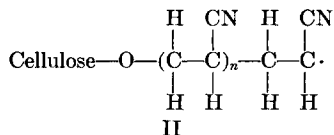
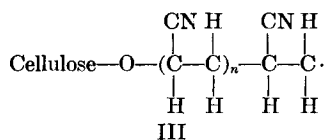


Fig. 3. ESR spectra of cotton cellulose I generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system plus acrylonitrile, recorded at  $-110^\circ\text{C}$ . ( $\times 5000$ ).

hydrogen atoms from carbon  $\text{C}_1$  or  $\text{C}_4$ .<sup>23</sup> The line width of this narrower singlet spectrum is about equal to that of the singlet spectrum resulting on depolymerization of cellulose by heat,<sup>7</sup> light,<sup>1,2</sup> or ionizing radiation.<sup>5,6</sup> The broader singlet spectrum probably resulted from the radical on the end of the growing polyacrylonitrile chain (II):



If the growing polyacrylonitrile chain occurred (III),



a triplet spectrum would have resulted.

The ESR spectrum generated in cotton cellulose I during the graft copolymerization reaction at  $-40^\circ\text{C}$ . and recorded at different power levels is shown in Figure 4. Increasing the attenuation from 10 db. (Fig. 4A) to 13 db. (Fig. 4B) increased the resolution of the spectrum. A shoulder on the spectrum recorded at 10 db. was resolved to indicate a weak line at 13 db. The ESR spectrum generated in cotton cellulose II, also during the graft copolymerization reaction at  $-40^\circ\text{C}$ ., is shown in Figure 5 and is almost identical to that generated in cellulose I. It would appear that lattice type did not influence the mechanism of the abstraction of hydrogen atoms from the cellulose molecule and the graft copolymerization reaction.

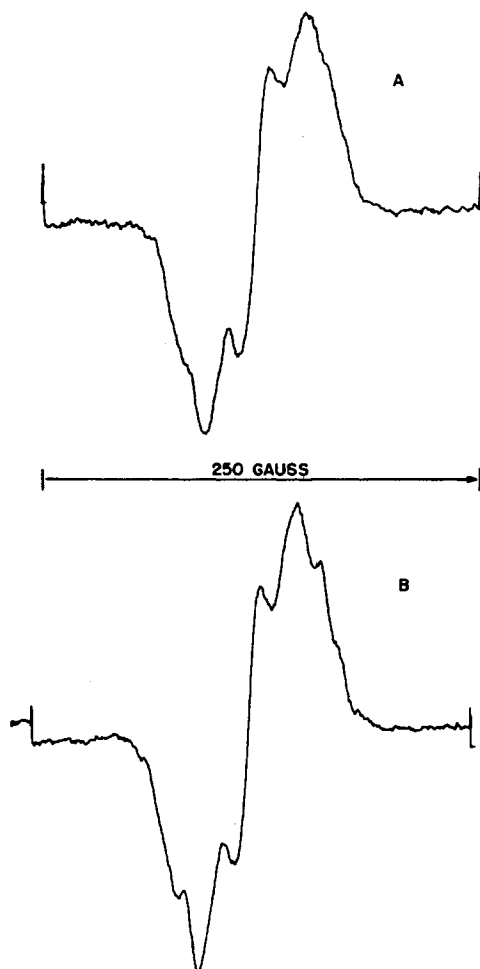


Fig. 4. ESR spectra of cotton cellulose I generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system plus acrylonitrile, recorded at  $-40^\circ\text{C}$ . ( $\times 2500$ ): (A) attenuation 10 db.; (B) attenuation 13 db.

The ESR spectrum generated in microcrystalline cellulose during the graft copolymerization reaction and recorded at  $-100^\circ\text{C}$ . is shown in Figure 6. The spectrum was less intense than those generated under the same conditions for cellulose I (Fig. 4) and cellulose II (Fig. 5). However, the ESR spectra and the line widths, generated for all three celluloses under the same conditions, were about the same. This indicated that the mechanism of hydrogen atom abstraction from the cellulose molecule and graft copolymerization were not dependent on molecular weight of the cellulose or lattice type.

The effect of temperature on the formation of free-radicals during the copolymerization of acrylonitrile with cotton cellulose I, initiated by the





Fig. 5. ESR spectra of cotton cellulose II generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system plus acrylonitrile, recorded at  $-40^\circ\text{C}$ . ( $\times 2500$ ).

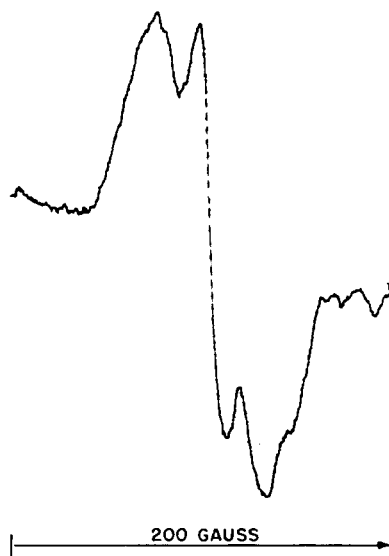


Fig. 6. ESR spectra of microcrystalline cellulose generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system plus acrylonitrile, recorded at  $-100^\circ\text{C}$ . ( $\times 19,300$ ).

$\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system, is shown in Figure 7. The cellulose was wet with  $0.1M$   $\text{FeSO}_4$  and then dried in a stream of nitrogen.  $0.03M$   $\text{H}_2\text{O}_2$ , saturated with acrylonitrile, was drawn onto the cellulose and immediately immersed in liquid nitrogen. At  $-70^\circ\text{C}$ . or below the concentration of free radicals was relatively stable. When the temperature was increased above  $-70^\circ\text{C}$ ., the free radical concentration increased with time, probably indicating that

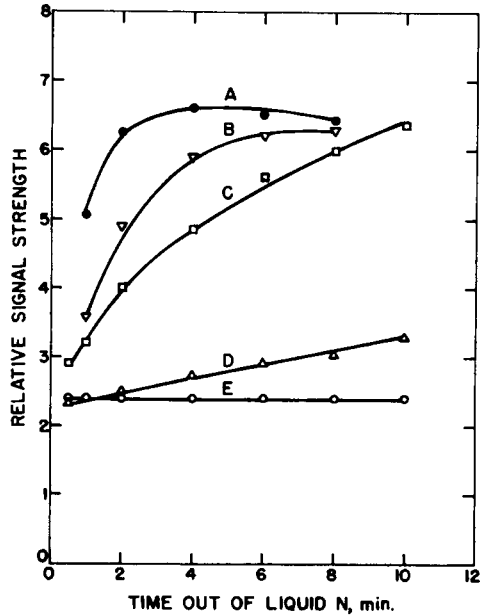


Fig. 7. Effect of temperature on the formation of free radicals during the copolymerization of acrylonitrile with cotton cellulose I generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system: (A)  $-30^\circ\text{C}$ .; (B)  $-40^\circ\text{C}$ .; (C)  $-50^\circ\text{C}$ .; (D)  $-60^\circ\text{C}$ .; (E)  $-70^\circ\text{C}$ .

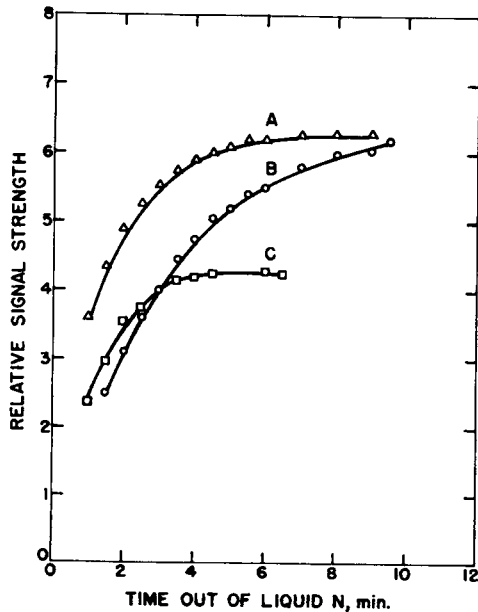


Fig. 8. Comparison of the concentration of free radicals formed in (A) cotton cellulose I, (B) cotton cellulose II, and (C) microcrystalline cellulose during copolymerization with acrylonitrile generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system at  $-40^\circ\text{C}$ .

the graft copolymerization reaction was occurring. Above  $-40^{\circ}\text{C}$ . the free radical concentration approached a maximum value.

A comparison of the rate of free-radical formation in cellulose I, cellulose II, and microcrystalline cellulose during copolymerization with acrylonitrile, generated by the  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  system at  $-40^{\circ}\text{C}$ ., is made in Figure 8. The concentration of free radicals in the celluloses approached a maximum value. In the case of cellulose I and II the maximum values were about the same. The maximum value for microcrystalline cellulose was less than those for cellulose I and II.

Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers. M. S. Bains is a resident postdoctoral research associate.

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