

19. Photochemistry of Cellulose. (III)

Effect of Wavelength under Consideration of Effect of Oxygen.

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The chromatic dependence in the photodegradation of cellulose by ultraviolet rays was observed under consideration of oxygen effect. As the light source, a low vapor pressure mercury arc lamp was employed.

The foreground of interest is the determination of effective spectral region for the photolysis of cellulose. It was found, under the present conditions of experiments, that the rays having wavelengths greater than 3000 Å showed no practical influence upon cellulose whose degradation was measured by cuprammonium D. P. On the other hand, cellulose was intensely affected by the rays having wavelengths smaller than 3000 Å.

The rays radiated from the mercury lamp in the spectral region below 3000 Å are mainly composed of two groups of lines whose centers are situated at 2537 Å and 1850 Å respectively. Of interest is the comparison of effects these line groups. The line group of 1850 Å can be cut off by a filter of 0.5% acetic acid solution having thickness of 1 cm. The filter transmits all other rays. Therefore, the irradiation through this filter represents the effect of 2537 Å only, while the bare rays bring about the summed effect of two groups, namely 2537 Å + 1850 Å. The effect of 1850 Å alone can be estimated by subtracting the effect of 2537 Å from the summed effect.

D. P. — time of exposure curves were obtained using oxygen pressure as a parameter. It was found that the degrading effect of 2537 Å is enhanced by increasing the oxygen pressure. This suggests that oxygen participates in the photolytic degradation of cellulose by the rays having greater wavelengths. On the contrary, the effect of 1850 Å was apparently decreased by increasing the pressure of oxygen. The negative effect of oxygen at the irradiation by 1850 Å may possibly be ascribed intensity diminution of the light due to the absorption by oxygen. When the intensity decrease is corrected by the Lambert-Beer's law, the degradation per unit light intensity is almost independent of oxygen pressure.

These results may represent the possibility that the primary process of 1850 Å upon cellulose would be the primary dissociation, while the rays of 2537 Å would produce primarily the photochemical activated molecules which are degraded by the ensuing action of oxygen.

20. Fundamental Studies on Cooking of Wood. (IV)

Soda Cooking