Study of the Relation between Brightness Reversion and Carbonyl Content in Cellulose Pulp

INGVAR JULLANDER and KURT BRUNE

Research Laboratory, Mo och Domsjö AB, Örnsköldsvik, Sweden

Giertz[1] in a study of the brightness reversion of pulp upon heating, found for sulfite pulps a reasonably good correlation between the brightness reversion during heating and carbonyl content (copper number) as well as carboxyl content.

The discovery and subsequent commercial manufacture of the strong reducing agent sodium borohydride has given the cellulose chemist means to reduce the carbonyl groups in carbohydrates to alcohol groups. Treatment of pulp with sodium borohydride results in improved hot alkali stability and sometimes slightly increased viscosity[2,3]. Recently Giertz and McPherson[4] in connection with a study of the coloring matter formed when pulp is heated, also reported an experiment where partial borohydride reduction of an overbleached sulfite pulp resulted in reduced brightness reversion.

The aim of the present work was to investigate further the connection between carbonyl content (measured as copper number) and brightness reversion. Even a complete reduction of pulp can be made under mild experimental conditions. It is therefore unlikely that any other undesirable changes take place in the pulp.

Air-dried pulp was defibrated with a mechanical stirrer in water into which sodium borohydride had been dissolved in amounts corresponding to 0.1—10 % calculated on the pulp. Pulp concentration 2 %. The mixture was kept at 50°C for 3 h. The slightly alkaline solution was then sucked off on a Büchner funnel, the cellulose pulp washed several times with water, then acidified with acetic acid and finally washed again with water to a pH of around 6.5. Drying in air at room temperature.

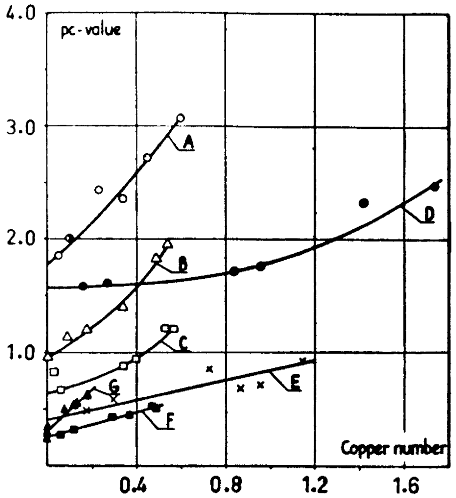

Fig. 1. Brightness reversion (pc-value) as a function of copper number for different types of pulp.

A, B and C — bleached sulfate paper pulps from pine.
D — bleached sulfite paper pulp from spruce.
E — bleached sulfite pulp from spruce, dissolving grade.
F — bleached, cold-alkaline treated sulfite pulp from spruce.
G — bleached cotton linters.

Copper number was determined according to Braidy[5]. Pulp sheets were formed and brightness measurements performed in an Elrepho instrument. The brightness reversion was calculated by means of the Kubelka and Munk theory as recommended by Tongren[6], Mc Intyre[7] and Giertz[1] and by the last author expressed as "post-color" value (pc-value). The pc-value can be regarded as a relative measure of the amount of coloring substance formed during the heat treatment.

On each curve in Fig. 1 the point with the highest copper number corresponds to pulp treated only with water in blank experiments. The carbonyl content was then reduced by increasing amounts of sodium borohydride down to such low values as to allow an extrapolation to copper number zero.

It can be seen that the carbonyl groups on an average are responsible for approximately half the brightness reversion. In the cases studied so far, the slope of the curves seems to be higher for sulfate pulps and linters than for sulfite pulps, but the experimental material is too scanty to allow a conclusion that this applies to all types of sulfite and sulfate pulps. Highly refined sulfite pulp is at least as good as linters as far as brightness stability is concerned, in spite of the higher copper number.

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Aliphatic Ditellurides

GÖRAN BERGSON

Chemical Institute, University of Uppsala, Sweden

Only two aliphatic ditellurides are described in literature; ditellurium-diacetic acid ($HOOCCH_2TeTeCH_2COOH$) and ditellurium-α-dipropionic acid [1,2]. These substances have been prepared by reduction of the trichlorotellurium compounds obtained by the interaction of tellurium tetrachloride with the corresponding acid anhydrides. This method seems to be suited only for the introduction of the tellurium function in the α-position relative the carboxylic group.

The author has started an investigation of synthetic methods for aliphatic ditellurides in general. This paper gives a preliminary report of the reaction between aliphatic halogen compounds and the Te_2^{2-} ion. The first electronic excitation band for di-n-butylditelluride and ditellurium-diacetic acid has been determined and compared with that for disulfides and diselenides extensively studied by Schotte [3,4] and Bergson [5,6]. An infra-red investigation of the ditellurides is being prepared. A polarographic investigation of ditellurium-diacetic acid has been started by Nygård [7].

A sodium ditelluride solution was prepared by dissolving finely powdered tellurium in an alkaline solution of sodium formaldehyde sulphoxylate (Rongalite C). When excess Rongalite C is used for the preparation of sodium telluride solution the tellurium is readily dissolved [8], but in the preparation of sodium ditelluride the molar ratio between tellurium and Rongalite C must be 2:1, and it is then necessary to reflux and to stir the mixture for several hours. The sodium ditelluride solution (which certainly contains also some telluride and polytelluride) reacts readily with n-butyl bromide. An attempt to prepare ditellurium-diacetic acid in this way from chloroacetic acid failed, because this acid oxidized the ditelluride ion to elementary tellurium, and from the reaction mixture acetic acid was isolated. Sodium telluride reacts in the same way with chloroacetic acid. Here we have a difference between tellurium, selenium and sulfur, because disulfide-, sulfide-, diselenide- and selenide ions react in the normal way with α-haloacids. These facts should be compared with the oxidative action of *vic*-dihalides on selenoles [9,10] contrary to their behavior towards thiols, and with the oxidation of sodium disulfide by bromomalonic ester [11].

Di-n-butylditelluride has an absorption band with maximum at 3 990 Å as can be seen from Fig. 1. The author has shown that the lowest electronic excitation energy for disulfides and diselenides can be expressed by an empirical formula with the parameters a and β:

$$E = a\sqrt{k} + \beta$$

with $a_S = a_{Se}$, where k is the number of hydrogen atoms joined to the α-carbon atom [6]. The author hopes to be able to test the validity of this relation for ditellurides. An increase in excitation energy is found when the molecule contains a carboxylic group close to the S—S or Se—Se group. For diselenium-diacetic acid ($HOOCCH_2SeSeCH_2COOH$) the band is overlapped by a high intensity band (λ_{max} = 2 290 Å) and is only detectable [5] as an inflexion at 2 930 Å. The same behavior has been found for ditellurium-diacetic acid (inflexion at 3 600 Å). The 2 290 Å band of the selenium compound has its correspondence in a band with λ_{max} = 2 730 Å.