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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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OXIDATIVE DECOMPOSITION OF CELLULOSE ETHERS

(Presented by Academician V. A. Kargin, November 28, 1956)

Cellulose ethers in the form of films, coatings, and other products, under the influence of the atmosphere and heating, lose elasticity and mechanical strength, which is associated with the active role of oxygen ($^{1-4}$). In this article some results are reported from studies of the oxidation of cellulose ethers by molecular oxygen.

Cellulose ethers, and the cellulose from which they were prepared, were heated (not above 200°) in a vessel with a porous bottom in a stream of air, oxygen, and inert gas. To take account of oxygen absorption, the oxidation of ethers was carried out in a closed system with internal circulation of the gases through absorbers in order to purify the oxygen from volatile reaction products.

Fig. 1. Thermo-oxidative decomposition of cellulose ethers: I and I'—characteristic viscosity of acetylcellulose at 200° (I—in nitrogen, I'—in oxygen); II and II'—the same at 140° (II—in nitrogen, II'—in oxygen)

Fig. 2. Rate of oxygen absorption during oxidation of ethylcellulose at 130° (per 1.5 g of ethylcellulose)

These experiments confirm that the cause of the thermal decomposition of cellulose ethers lies in their oxidation by oxygen (Fig. 1).

The rate and degree of destruction can be judged both from the change in viscosity of cellulose-ether solutions and from the amount of absorbed oxygen and volatile oxidation products. Oxygen absorption is usually characterized by integral-type curves (Fig. 2).

The oxidation reaction of cellulose ethers by oxygen is characterized by the presence of induction periods, the duration of which depends on the temperature and the periods of prior storage of the ether. During oxidation of cellulose ethers, their degree of polymerization decreases, ether groups are split off,

groups, and carbonyl and carboxyl groups arise in the ester molecule.

Aging and thermooxidative decomposition of ethylcellulose. Technical ethylcellulose was studied, purified and reprecipitated (under a constant precipitation regime), with an ash impurity content of about 0.01%.

Ethylcellulose is slowly oxidized by oxygen even at room temperature; peroxide groupings arise in its molecule and acetaldehyde is liberated.

If the peroxide groups in samples of ethylcellulose that have been stored for a long time are decomposed, induction periods of oxidation reappear; these are absent in samples stored for a long time (Fig. 3).

Fig. 3. Effect of peroxide groups in ethylcellulose on the rate of its thermooxidative decomposition (at 130°): *I* –intrinsic viscosity one month after preparation of the sample, *II* –the same, after two years, *III* –the same, after removal (decomposition) of the peroxide groups.

The thermooxidative decomposition of ethylcellulose reaches a high rate at 125–140° and is accompanied by the formation of liquid and gaseous products: acetaldehyde (the principal product), ethyl formate, ethyl alcohol, formic acid, carbon dioxide, and, when samples containing up to 0.5% ash are oxidized, methylglyoxal is also formed in small amounts. All the indicated products were isolated by fractional distillation on a vacuum column and characterized.

The amount of acetaldehyde and ethoxyl groups in the ethyl alcohol and ethyl formate formed in the reaction corresponds to a decreased percentage of ethoxyl.

The characteristics of ethylcellulose before and after oxidation are given in Table 1.

Table 1

Ethylcellulose	Yield, %	M.p., °C	$[\eta]$	Mol. wt., $1 \cdot 10^3$	Elemental composition, % C	Elemental composition, % H	Elemental composition, % O	Ethoxyl, %	Carboxyl, % total	Carboxyl, % uronic	Aldehyde groups, %	Carbonyl groups, %
Initial	–	185	1.65	45	56.77	9.09	34.14	47.1	0.11	0.05	no	no
Oxidized	93	125	0.11	–	54.47	8.36	37.16	36.9	–	–	–	–

Ethylcellulose	Yield, %	M.p., °C	$[\eta]$	Mol. wt., $1 \cdot 10^3$	Elemental composition, % C	Elemental composition, % H	Elemental composition, % O	Ethoxyl, %	Carboxyl, % total	Carboxyl, % uronic	Aldehyde groups, %	Carbonyl groups, %
a. Water-insoluble fraction (after dialysis)	64	134	0.12	2	–	–	–	38.0	1.35	1.0	2.7	0.2
b. Water-soluble fraction	27	83	–	–	–	–	–	31.7	6.6	2.1	6.5	0.3

Note. The total content of carboxyls was determined by potentiometric titration in alcoholic solution; aldehyde groups, by iodine numbers; molecular weight, by the sedimentation method in an ultracentrifuge; $[\eta]$ is the characteristic viscosity in acetone solution.

Spectral analysis also showed an increase in carbonyl and hydroxyl groups in the oxidized ethylcellulose.

Like ethylcellulose, methyl-, benzyl-, allylcelluloses and other simple ethers are oxidized by oxygen and undergo degradation with cleavage of ether groups and liberation, respectively, of formaldehyde, benzaldehyde, and acrolein as the principal reaction products.

Oxidation of Cellulose Esters. Cellulose esters are destroyed at higher temperatures. During the oxidation of acetylcellulose, one acetyl group is split off comparatively easily from the glucose unit in the form of acetic acid and acetaldehyde.

Cellulose esters of higher aliphatic acids—propionic and butyroacetic esters (containing 46% butyric and 18% acetic acid)—are oxidized differently. Propionic esters in this case liberate predominantly acetaldehyde and propionic acid, as well as acetic acid; acetobutyrates give a mixture of propionic, butyric, and acetic acids (in the ratio 6 : 2 : 1) and the corresponding aldehydes.

The acids and aldehydes were separated by fractional distillation and by chromatographic adsorption; the aldehydes were separated by means of their 2,4-dinitrophenylhydrazones.

In all cases, in the course of oxidation of the esters, carbon monoxide and carbon dioxide are evolved in a ratio of 1 : 2.

The oxidation of cellulose ethers by oxygen under irradiation with ultraviolet light proceeds in an analogous manner.

The oxidation process is also studied on esters of glucose and cellobiose, which, like cellulose esters, are cleaved at the ester groups with liberation of the corresponding volatile products.

The oxidation of cellulose esters and sugars is prevented by additions of antioxidants.

Conclusions

1. Aging and thermo-oxidative decomposition of cellulose ethers are a consequence of their oxidation by atmospheric oxygen, proceeding through the stage of formation and decomposition of peroxides.
2. During oxidation, the alkoxyl groups of simple ethers are split off in the form of the corresponding aldehydes and alcohols, while ester groups are split off in the form of the acids constituting the esters, as well as acids and aldehydes with one fewer C atom than in the acid group of the ester.
3. In the molecules of ethers, as ether groups are split off, carboxyl and carbonyl groups accumulate.

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References Cited

1. S. N. Danilov, O. P. Kozmina, *ZhOKh*, **18**, 1823 (1948).
2. L. F. McBurney, E. F. Evans, Ind. and Eng. Chem., **41**, 1251, 1260 (1949).
3. A. A. Freiman et al., *ZhPIKh*, **24**, 490 (1951); **25**, 626 (1952).
4. G. C. Decroes, I. W. Tamblyn, Modern Plastics, **29**, 127, 185 (1952).

Note: Figure translations are in progress. See original paper for figures.