

The Pyrolysis of Cellulose Derivatives

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Synopsis

The thermal degradation *in vacuo* of ethyl cellulose and cellulose acetate in the form of very thin films or bulk material between 230° and 320°C has been studied. With the ethyl cellulose films, volatilization (as measured by weight loss) was a first-order process up to about 50% reaction, with an activation energy of 208 kJ/mole. This is about the same as that associated with the initial drop in intrinsic viscosity of the solid during bulk pyrolysis, in which very high molecular weight material, probably crosslinked, was formed at a later stage. The volatile products from ethyl cellulose included H₂O, CO, CO₂, C₂H₄, C₂H₆, C₂H₅OH, CH₃CHO, unsaturated aliphatic compounds, and furan derivatives. Acetic acid and acetyl derivatives of D-glucose were produced from cellulose acetate. It is suggested that the polymers degrade by radical chain mechanisms, and a number of possible elementary steps are proposed.

INTRODUCTION

Whereas the products and mechanisms of the thermal decomposition of some polymers, e.g., polyformaldehyde and poly(methyl methacrylate), are relatively simple, many polymers, e.g., polyolefins and cellulose, degrade to give complex mixtures of compounds the mechanisms of formation of which are either unknown or insufficiently defined.¹ In contrast to the very extensive literature on the degradation of cellulose itself, there are comparatively few data on the pyrolysis of cellulose derivatives, particularly ethyl cellulose,² although cellulose triacetate has been studied by Scotney.⁹ As part of a study of the mechanism of polymer burning, we have investigated the kinetics and products of the pyrolysis of samples of ethyl cellulose (and also cellulose acetate), with the results reported here.

EXPERIMENTAL

The vacuum pyrolysis of the cellulose derivatives, in the form of thin films (cast on slides) or of larger samples contained in a suitable boat, was studied using the apparatus shown in Figure 1(a), which consisted basically of a thermoregulated air oven ($\pm 0.2^\circ\text{C}$), a pyrolysis tube, and a vacuum line. By use of the guided rod system, the smaller samples were introduced into the hot zone from the cool region of the pyrolysis tube under vacuum conditions.

Thin Films

For the kinetic experiments the thin films were cast on circular glass microscope cover slides from appropriate volumes of freshly prepared polymer solu-

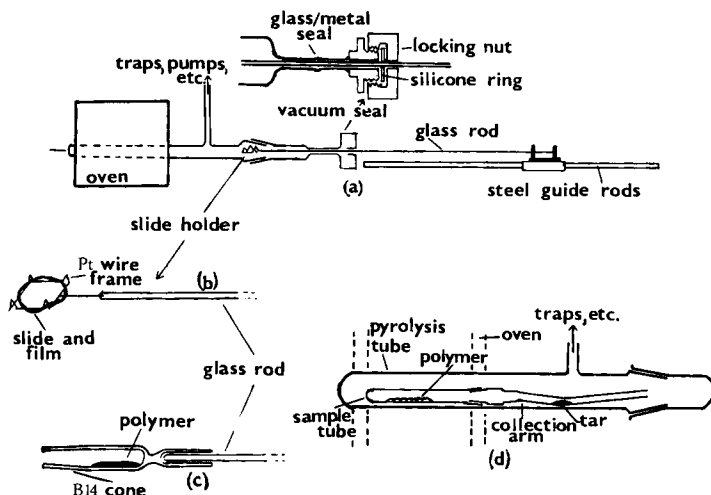


Fig. 1. (a) General apparatus for study of polymer degradation. (b) Slide holder (2–9 mg samples). (c) Boat (0.25 g samples). (d) Sample tube and collection arm (1–2 g samples).

tions, using as solvents benzene for ethyl cellulose and dioxan for cellulose acetate. The solvent was allowed to evaporate at room temperature and final traces driven off by heating the slides at 120°C for 6 hr *in vacuo*. The slides were weighed before and after casting the films. A 4-mg film had an average thickness of 10^{-3} cm. To determine the rate of weight loss, a slide was placed horizontally in the platinum wire frame, Figure 1(b), and the apparatus assembled as in Figure 1(a) so that the slide was situated in the cool region. The pyrolysis tube was evacuated and the slide was then pushed into the center of the hot zone. After an appropriate time the slide was withdrawn to the cool zone, removed after admission of air, and reweighed. The procedure was repeated with different pyrolysis times to obtain weight loss-versus-time data.

During the pyrolyses the most volatile degradation products pumped off were trapped at -196°C . At the end they were distilled into phials and analyzed by gas-liquid chromatography using a Carbowax 1540 column at 80° or 110°C.

Some undegraded and partly degraded films were extracted with benzene, recast on sodium chloride discs, and the infrared spectra obtained.

Molecular Weight Determination

To investigate changes in the molecular weight and molecular weight distribution of the solid during degradation of ethyl cellulose, the pyrolysis procedure was the same as for thin films except that the sample (approximately 0.25 g) was contained in a boat, Figure 1(c). The cool samples were either dissolved in benzene and the intrinsic viscosities obtained using an Ubbelohde viscometer or dissolved in tetrahydrofuran and analyzed by gel permeation chromatography in the Polymer Supply and Characterization Center at RAPRA, Shrewsbury.

Bulk Pyrolysis

For pyrolyses of 1- to 2-g samples of ethyl cellulose, the apparatus shown in Figure 1(d) was used. The sample tube and collection arm were placed in position, with the oven at room temperature. The whole was evacuated and the

oven rapidly heated to the pyrolysis temperature. The volatile products were either trapped as before or condensed as tar in the cool zone and were investigated by gas-liquid chromatography (using the Carbowax column and also a silicone MS 500 column at 130°–180°C, a molecular sieve 5A column at 80°C, and a Porosil B column at 25–80°C), infrared spectroscopy, mass spectrometry, and thin-layer chromatography.

Materials

One sample of ethyl cellulose powder (degree of substitution approximately 2.5) was obtained from BDH and another sample (N200 grade), from the Hercules Corporation. Cellulose acetate (D.S. 2.3) and cellulose triacetate were obtained from British Celanese and Phase Separations, respectively.

RESULTS

Kinetics of Weight Loss

Films of ethyl cellulose weighing 4 mg were pyrolyzed at temperatures between 268° and 320°C. There was a "warm-up" period of <100 sec, which was small compared to the pyrolysis times, and a nonvolatile residue of approximately 3% of the initial mass was left at the end. Some 2-mg and 9-mg films were also used. Figure 2 shows some typical results plotted according to the first-order expression

$$\log_{10} \left(\frac{100 - W_r}{R_s - W_r} \right) = \frac{kt}{2.303}$$

where R_s and W_r are the percentages of the initial mass of film remaining at times

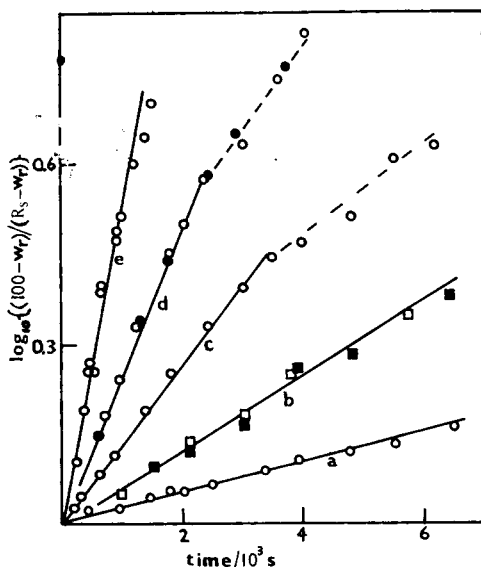


Fig. 2. First-order plots for the weight loss on pyrolysis of thin films of ethyl cellulose *in vacuo*. Initial mass of film, 4 mg, except for (●) 2 mg and (■) 9 mg. Temperature (°C): (a) 268; (b) 278; (c) 288; (d) 296; (e) 306.

t and ∞ , respectively. It can be seen that the process is first order over about 50% of the weight loss and that the mass (and therefore the thickness of the film) does not affect the rate within experimental error. The variation of the observed first-order rate coefficient k with temperature is shown in Figure 3, the overall activation energy being 208 ± 6 kJ/mole and the overall preexponential factor 7.3×10^{15} sec $^{-1}$.

Pyrolysis in 10 torr air considerably increased the rate of weight loss in the initial stages at 296°C, as did addition of 9% w/w lithium nitrate and basic lead acetate to the initial film, whereas lithium sulfate had no effect.

The Solid Phase

After 60% weight loss at 278°C, the infrared spectrum of a thin film of ethyl cellulose (initial mass 4 mg) showed a 63%–71% decrease in intensity of the absorption bands at (cm $^{-1}$) 1110 (C—O—C), 1380 and 1450 (CH $_3$), 2850 (C—H),

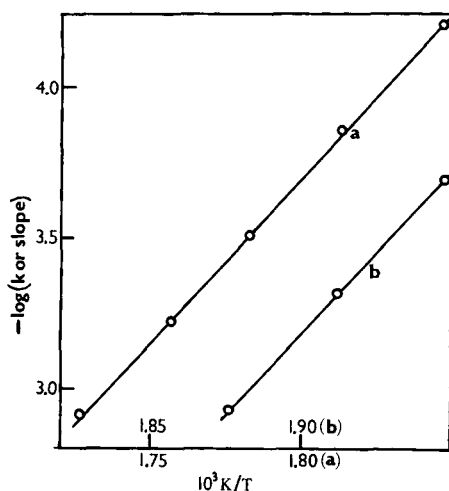


Fig. 3. Arrhenius plots of the variation with temperature of (a) the first-order rate coefficient k for the weight loss with thin films and (b) the initial slope of the plots of $[\eta]^{-1}$ vs time for the solid left (initial mass, 0.25 g) on pyrolysis of ethyl cellulose *in vacuo*.

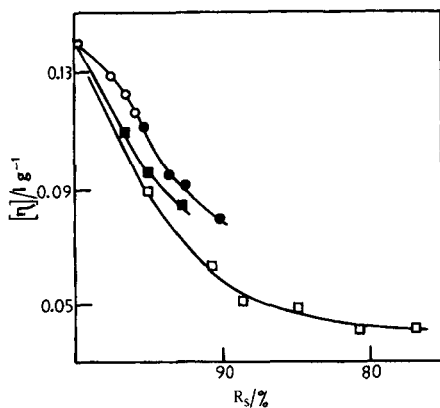


Fig. 4. Variation of the intrinsic viscosity of solid left with percentage of initial mass remaining on pyrolysis of 0.25 g ethyl cellulose *in vacuo*. Temperature (°C): (○) 230; (●) 240; (■) 250; (□) 260.

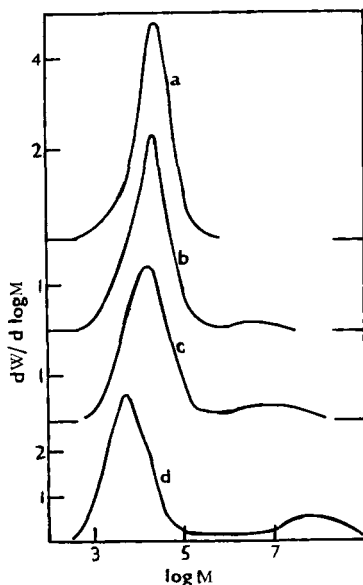


Fig. 5. Typical molecular weight distribution curves for the solid left in the pyrolysis of ethyl cellulose (initial mass 0.25 g) at 260°C. % Weight loss: (a) 0; (b) 4.8; (c) 11.2; (d) 19.4.

and 3450 (O—H). There was probably slight loss of material during transfer of the pyrolyzed film (see experimental section). The infrared spectrum of a film pyrolyzed in air showed prominent absorption bands at 1640 (C=C) and 1740 cm^{-1} (C=O). With cellulose acetate (D.S. 2.3) the percentage decrease in the C=O, C—H, and O—H absorption was approximately the same as the percentage weight loss for a 4-mg film pyrolyzed at 354°C.

The number-average molecular weight of the BDH ethyl cellulose determined by osmometry, $(3.52 \pm 0.15) \times 10^4$ g, agreed within experimental error with the value, 3.87×10^4 , obtained from the intrinsic viscosity using the Mark-Houwink constants given by Moor and Brown.³ The intrinsic viscosity decreased rapidly at first on pyrolysis but became constant after only about 20% weight loss, and insoluble material was formed (Fig. 4). The Huggins constant fell to nearly zero, all the values at the various temperatures lying on the same line. Plots of $[\eta]^{-1}$ versus time were linear in the early stages of the degradation, and the variation of the initial slope with temperature (Fig. 3) gave an overall activation energy of 204 kJ/mole.

Typical molecular weight distribution curves obtained by gel permeation chromatography for the pyrolysis of the ethyl cellulose of 260°C are shown in Figure 5. The distribution ($\log M < 5.5$) shows a shift to lower molecular weights as pyrolysis proceeds, but a material with $\log M > 5.5$ was formed. The ratio of the weight-average to the number-average molecular weight, \bar{M}_w/\bar{M}_n , increases from 2.7 to 4,100.

Volatile Products

The products from the degradation at 306°C of the thin films of ethyl cellulose, collected at -196°C , were mainly water, ethanol, and acetaldehyde with some

carbon dioxide, ethane, and ethylene, but represented only about 20% w/w of the total volatiles calculated from the weight loss. The yields were approximately proportional to the total amount volatilized at any time (Fig. 6). With cellulose acetate films the main volatile product was acetic acid, but some water was again formed.

The volatile products from the bulk degradation of ethyl cellulose at 260°–290°C were separated into three fractions: (a) a tar, nonvolatile at room temperature, see Figure 1(d); (b) a liquid fraction boiling above room temperature at atmospheric pressure; and (c) a gaseous fraction condensing below room temperature. The yield of tar at 280°C increased from 31% to 50% w/w of the total volatiles as degradation proceeded, the final liquid and gas yields being 36% and 14%, respectively. Although giving high yields of tar on degradation, the nonvolatile residue after 50% weight loss was insoluble in solvents such as benzene, methanol, chloroform, and tetrahydrofuran.

The tar was yellow brown, and the infrared spectrum showed strong absorption bands at about (cm^{-1}) 1650 (C=C), 1740 (C=O), and 3490 (O—H). Separation by thin-layer chromatography showed the presence of several components one of which with sulfuric acid gave a green color characteristic of furan compounds. A methanol solution of the tar gave a precipitate with 2,4-dinitrophenylhydrazine. Thin-layer chromatography indicated the presence of at least two components one of which may have been the derivative of diacetyl.

The liquid fraction was acid and gave a precipitate with 2,4-dinitrophenylhydrazine. Thin-layer chromatography showed the presence of at least five hydrazones, including possible those of diacetyl and methyl ethyl ketone. The infrared spectrum of the liquid showed a series of bands between 1600 and 1850 cm^{-1} , corresponding to the olefinic and carbonyl absorption regions. Mass spectrometry indicated the presence of water, ethanol, acetaldehyde, unsaturated hydrocarbons, aldehydes, ketones, and ethers, and a number of furan derivatives, including furfuraldehyde and furfuryl alcohol. Gas chromatography showed that ethanol and water were the main components of the fraction, with less acetaldehyde, formic acid, methyl formate, acetone, furfuraldehyde, and at least eight unidentified compounds.

The main components of the gas fraction were CO, CO₂, C₂H₄, and C₂H₆, with a little CH₄ and traces of C₃H₆, C₃H₈, C₄H₈, and C₄H₁₀.

The tar from the bulk degradation of cellulose acetate (D.S. 2.3) was shown to contain acetyl derivatives of D-glucose by acetylation with acetic anhydride/pyridine and analysis by gas-liquid chromatography. The α and β forms of D-glucose pentaacetate were present.

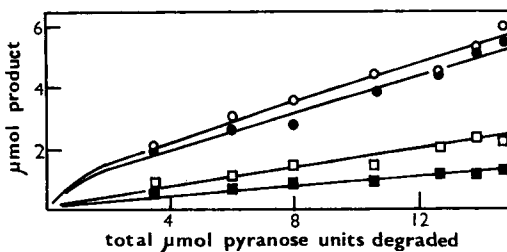


Fig. 6. Yields of volatile products from the degradation of thin films of ethyl cellulose at 306°C: (●) H₂O; (□) CO₂ + C₂H₄ + C₂H₆; (■) CH₃CHO; (○) C₂H₅OH.

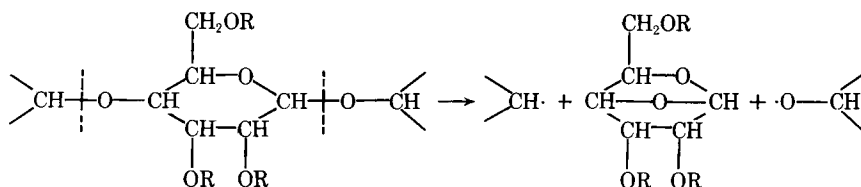
DISCUSSION

The rates of weight loss with the thin films of ethyl cellulose were independent of film thickness, indicating that there were no diffusion limitations. The overall activation energy is similar to those reported by Madorsky et al.⁴ for cellulose and cellulose triacetate, suggesting a similar degradation mechanism at least in the initial stages, although the initial rate of pyrolysis of ethyl cellulose was about 10 times that of the other polymers. Oxygen, lithium nitrate, and lead acetate would give rise to free radicals at 296°C, and their accelerating effect on the degradation suggests that it involves a radical mechanism.

During pyrolysis of the samples of ethyl cellulose for molecular weight studies, the depth of the molten layer was about 0.1 cm (100 times greater than that of the thin films), and the initial rates of weight loss were about one third of those for the thin films, indicating some diffusion limitation of volatilization. Nevertheless, the activation energy associated with the initial rapid viscosity decrease was the same (within experimental error) as that for the weight loss with thin films, suggesting that random chain scission is involved in the mechanism of volatilization although gel permeation chromatography showed no major shift to lower molecular weights until after about 10% reaction. However, in contrast to the thin film results, insoluble material is formed at a relatively early stage in the pyrolysis and a fraction of very high molecular weight (degree of polymerization of around 10^5) is formed. Probably crosslinking is taking place, as indicated by the sharp increase in \bar{M}_w/\bar{M}_n , due to the presence of volatile products, particularly tar, in the melt. Segel⁵ found that solutions of cellulose nitrate formed a gel on standing in air. The \bar{M}_w/\bar{M}_n ratio increased and high molecular weight material, degree of polymerization $\sim 10^5$, was formed.

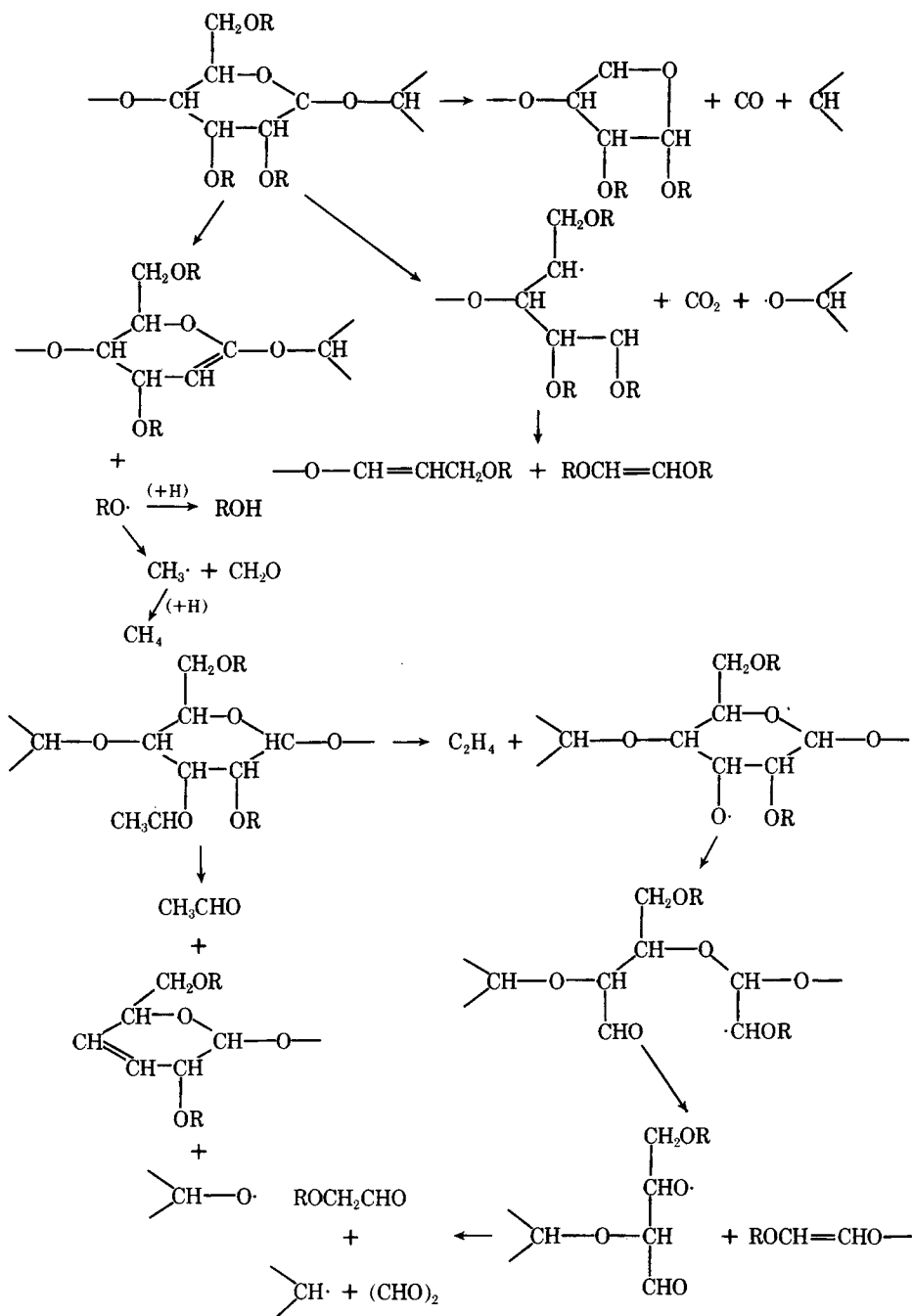
The ethanol, acetaldehyde, and ethane and probably (if not all) the ethylene produced are derived from the ethoxy groups in the ethyl cellulose. Although only a relatively small proportion of the C_2H_5O groups present in the original ethyl cellulose are evolved as ethanol (about 1 in 8 for thin films and 1 in 2.5 for the bulk polymer at 260°C), during the first 23% weight loss in the bulk pyrolysis at 260°C the sum of the yields of the four C_2 products accounts for about 80% of the ethoxy groups lost. However, in the later stages or with thin films this percentage is much smaller, and thus some structures containing ethoxy groups must be present in the other volatiles.

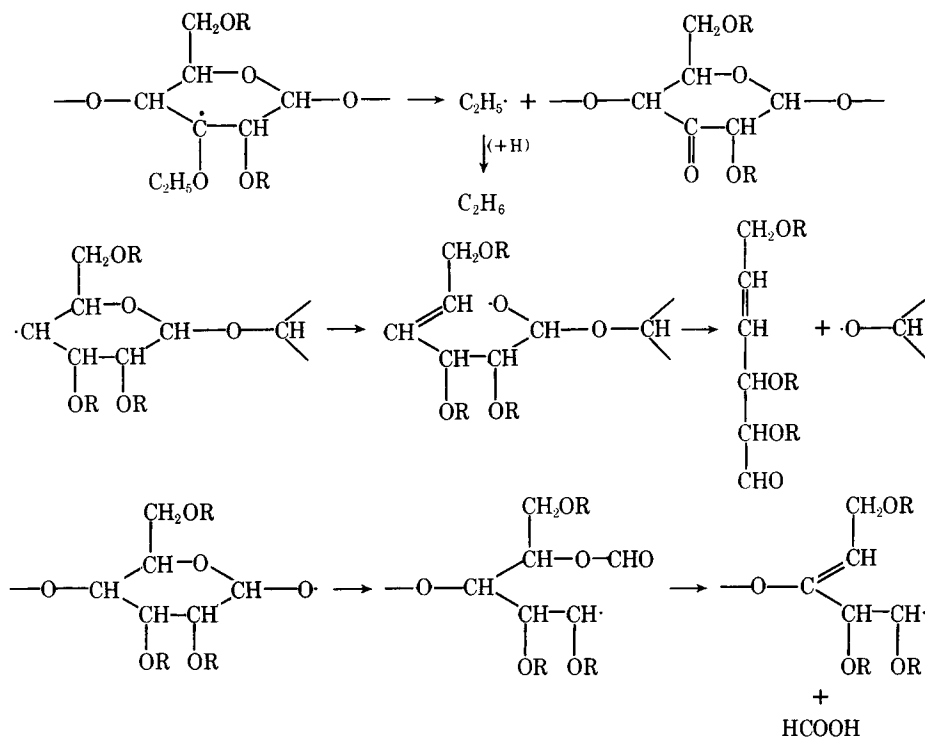
Saturated ethers decompose by free-radical chain mechanisms.⁶ With ethyl cellulose, initiation will be by fission of the relatively weak glycoside C—O bonds. This may be followed by depolymerization, viz. (where R = H or C_2H_5),



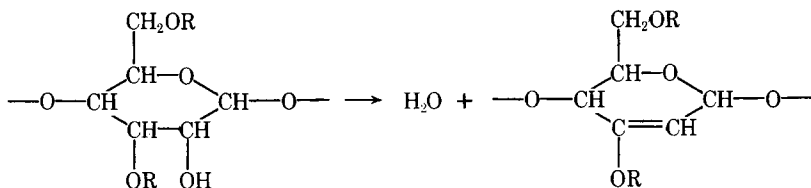
especially since trimethyl cellulose gives relatively high yields of trimethyl-1,4-anhydro- β -D-glucopyranose on pyrolysis.¹ However, in the melt, small

radicals (e.g., C_2H_5O) will abstract hydrogen, either from the ring or from the side groups (since such processes have low activation energies, 20–40 kJ/mole)⁷ forming macroradicals, which will decompose to give the various volatile products; and fragmentation of the polymer chains may occur propagating the reaction, e.g., scheme 1 ($R = H$ or C_2H_5):



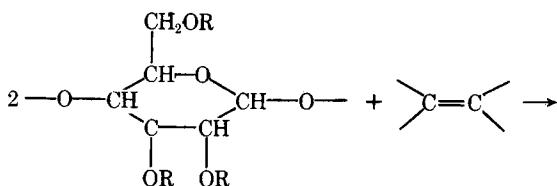


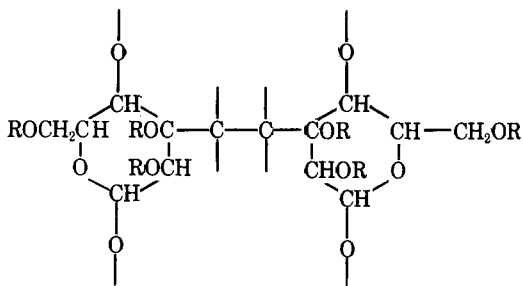
Water is formed from hydroxyl radicals by hydrogen abstraction but may also be produced by the dehydration reaction



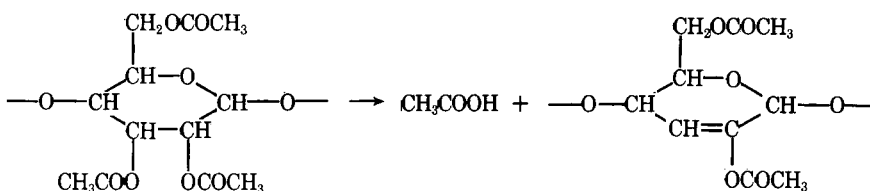
which occurs readily in the pyrolysis of cellulose above 220°C.^{1,8}

Termination probably occurs by combination (or disproportionation) of macroradicals, but crosslinking of the polymer chains appears to be prominent only with the thicker melts and is probably due to the presence of unsaturated species to which macroradicals can add, for example,





With cellulose acetate, most if not all of the acetic acid is probably formed by *cis*-elimination involving a β -hydrogen atom, for example⁹



as with other acetate esters containing the $\text{CH}_3\text{COOC}-\text{CH}$ moiety.⁶ Also CH_3CO_2 radicals, if produced, would decompose rather than abstract hydrogen since they are very unstable⁶ above about 100°C . Otherwise, the elementary processes occurring in the pyrolysis are likely to be similar to those with ethyl cellulose, and have been discussed by Scotney.⁹

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