excess of phenylacetylene, yielded no recovered 2-pyrone, and compounds **8** (14%) and **9** (12%) were obtained in approximately equal amounts from 1.2 g (80%) of crude product.

Polymerizations. (See Table I.) Equimolar amounts of compounds **4** or **5** and diethynylbenzene[14] were combined with 10 ml of reagent grade toluene in 20-ml polymerization tubes. The tubes were fitted with septa and subjected to three freeze–thaw cycles (liquid nitrogen) before being sealed under reduced pressure. Each tube was heated at 200–300° in a Parr bomb containing 50–75 ml of toluene for 24–176 hr. Heat was supplied by an electric mantle, the temperature being controlled by a Jelrus automatic controller connected to a thermocouple in the bomb head. Polymers were precipitated by filtering the toluene solutions from the tube into acetone and/or petroleum ether (bp 30–60°) and were freeze-dried from benzene prior to characterization. Intrinsic viscosities were taken in toluene at 30°.

The highest molecular weight polymer ($[\eta] = 0.130$) was submitted for elemental analyses.

Anal. Calcd for $(C_{48}H_{32})_n$: C, 94.74; H, 5.26. Found: C,90.95; H, 5.24.

Compound $C_{23}H_{16}O_2$. 4,5,6-Triphenyl-2-pyrone (1.0 g, 3.0 mmol) and 10 ml of toluene were heated at 250° for 48 hr in a polymerization tube sealed in the usual manner. Cooling crystallized 0.77 g of starting material. Evaporation of solvent and extraction of the residue with methanol left another 0.06 g of starting material, identified by its non-depressed melting point on mixing with 4,5,6-triphenyl-2-pyrone. Concentration of the methanol solution and addition of water to turbidity, followed by cooling, precipitated a solid, 0.122 g, mp 200–202°, after recrystallization from methanol–water.

Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.19; H, 4.93. Found: C, 85.27; H, 5.10.

The same compound was isolated from attempted reactions of 4,5,6-triphenyl-2-pyrone with benzonitrile, terephthalonitrile, and 3-chloronitrile under similar conditions.

The Degradation of Methylcellulose by Ionizing Radiation

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ABSTRACT: The degradation of methylcellulose in the solid state, induced by ionizing radiation, has been studied under a variety of conditions. Application of the theory of random chain fracture to the experimental results, along with consideration of the rate of formation of various species during the degradation, leads to several interesting conclusions regarding the mechanism of the degradation. The reaction behaves in a manner consistent with a short-chain, free-radical mechanism resulting in concurrent fragmentation and ester formation.

Although there are many reports in the literature dealing with the effects of ionizing radiation on cellulosic materials, there are relatively few which are concerned with the detailed mechanism of the over-all reactions.

The radicals formed in cellulose by ionizing radiation have been tentatively identified by means of esr spectroscopy[1] as a mixture of secondary carbon radicals and tertiary alkoxy radicals. It was also observed by these workers that the esr spectrum due to these species slowly changed into a spectrum containing relatively greater amounts of alkoxy radicals. In methylcellulose, a similar situation was observed, with a *G* value[2] for radical formation of approximately 0.8 radicals/100 eV.[1a] In cellulose, the *G* value for radical formation was calculated to be 0.9[1b] and 0.8–3.0,[1a] depending upon the type of cellulose and its physical state. The rate of production of radicals in cellulose has been found to follow an empirical relationship,[1b] $(\mathrm{R}\bullet) = b\ (\text{dose})^a$,

Several attempts have been made to relate the rates of various reactions to the rate of energy deposited in a cellulosic system. Qualitatively, both the rate of radical disappearance and the rate of chain cleavage in cellulose have been observed to be faster in the presence of oxygen, although in both instances the differences were not great.[1b,3] Attempts at a more quantitative investigation of the rate processes involved have been made.[4-6] Several different rate laws for destruction of chain linkages in cellulose have been reported. Arthur[4] has proposed an equation of the type

$$\ln (P) = k_1 \ln (N_n) + K \tag{1}$$

where P is the number of chain fractures and N_n is the total dose delivered to the system. Equation 1 is essentially the same as that derived by Charlesby,[5] who envisaged the degradation of cellulose as a random chain fracture process, leading to the relationship

$$\ln (\eta) = \frac{1}{\alpha} \ln (D + D_0) + K \tag{2}$$

in which D_0 represents the dose necessary to degrade a polymer molecule of infinite molecular weight to a molecular weight equivalent to that of the starting ma-

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(1) (a) R. E. Florin and L. A. Wall, *J. Polym. Sci., Part A*, **1**, 1163 (1963); (b) S. Dilli, I. T. Ernst, and J. L. Garnett, *Aust. J. Chem.*, **20**, 911 (1967).

(2) *G* values are defined in terms of occurrences per 100 eV of absorbed energy.

(3) J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, *Amer. Dyestuff Reptr.*, **49**, 383 (1960).

(4) J. C. Arthur, Jr., *Textile Res. J.*, **28**, 204 (1958).

(5) A. Charlesby, *J. Polym. Sci.*, **15**, 263 (1955).

(6) M. Horio, R. Imamura, and H. Mizurkami, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 17 (1963).

terial, D is the dose delivered to the system and η is the resulting intrinsic viscosity. Empirically, Horio, Imamura, and Mizurkami[6] found that a relationship of the type

$$\ln (DP) = k \ln (\text{dose}) + K \tag{3}$$

was a satisfactory representation of their results on the study of cellulose degradation by ionizing radiation.

The energy necessary to produce a chain cleavage in cellulose has been calculated to be 9 eV[5] while in methylcellulose a value of 21.8 eV has been reported.[7]

Gaseous product analysis of radiation-degraded cellulose has shown the presence of H_2, CO, CO_2 and CH_4,[7,8] although there is some disagreement as to the relative abundances of the above species. Analysis of the degraded polymer for functional groups resulting from irradiation has shown the presence of acids,[9] carbonyls[6,9] and formate esters.[6] Blouin and Arthur were able to correlate the number of carboxylic groups formed with the number of chain fractures, obtaining values of 1.28 carboxylic groups per fracture in the presence of oxygen and 0.83 carboxyls per fracture in the presence of nitrogen.[9]

The work reported here represents an attempt to arrive at a more detailed conclusion regarding the mechanistic pathway which leads to the destruction of chain linkages in a methylcellulose polymer.

Experimental Section

Methylcellulose. The alkylated cellulose used in this study was a commercial variety, designated Methocel 60 HG, obtained from the Dow Chemical Co., having an average degree of methoxyl substitution of 1.87 and an average degree of hydroxypropyl substitution of 0.25. The material was used in four different states of initial molecular weight, designated in terms of its 2% solution viscosity. These values were nominally 4000, 400, 50 and 10 cP.

Irradiations. Irradiation of the various samples was carried out by placing known amounts of the cellulosic material in the form of a fine powder in loosely capped 2- or 4-oz bottles, and then placing these bottles in the radiation field of a cave facility containing a nominally 18,000-Ci cobalt-60 γ source. In those instances where the effects of water and/or air were being investigated, the reactions were run in sealed glass ampoules. Dose rates were measured by using ferrous sulfate dosimetry[10] in identical bottles. Correction for differences in absorbed dose rate between the dosimeter solution and the cellulose derivative was accomplished by conventional techniques.[11]

Determination of Molecular Weight. The 2% solution viscosity of methylcellulose was measured using standard techniques[12] while the number-average molecular weight was determined by means of a Mechrolab 501 membrane osmometer. In order to facilitate the determination of the molecular weight of the irradiated samples, a plot of the logarithm 2% solution viscosity *vs.* the logarithm of number-average molecular weight was constructed. The plot was linear, and allowed the conversion of 2% solution viscosity directly into the number-average molecular weight.

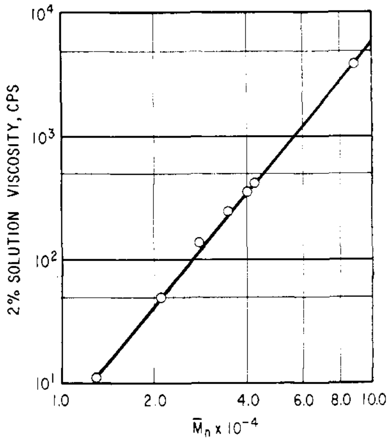

Figure 1. Relationship between solution viscosity and number-average molecular weight.

Functional Group Analysis. The analysis of the irradiated cellulose derivatives for two functional groups (carboxy and carboalkoxy) was carried out in a straightforward manner by titration with 0.1 *N* NaOH in the case of carboxy determination, and by hydrolysis with 1.0 *N* NaOH followed by back titration with 1.0 *N* HCl in the case of carboalkoxy determination.

Results and Discussion

The degradation of cellulose in the solid state by ionizing radiation can be treated as a process consisting of random chain fractures.[5] Of the several mathematical techniques which can be utilized in analyzing such a process we have chosen to take a kinetic approach.

Assume first that the process of breaking a bond in the polymer structure is independent of the location, number and/or nature of the bonds. Then

$$-\mathrm{d}N/\mathrm{d}t = kI^x \tag{4}$$

where N is defined as the number of bonds per gram which when destroyed will result in the splitting of one polymer molecule into two, I is the intensity of impinging radiation and x is some number less than or equal to one. Integration leads to

$$N_0 - N = kI^x t \tag{5}$$

The number of bonds that can be broken in a sample (N_i) can be related to the number-average molecular weight (M_n)

$$A/M = \text{molecules per gram}$$

$$M_n/M - 1 = \text{bonds per molecule}$$

$$(A/M_n)(M_n/M - 1) = (A/M) - (A/M_n) =$$
$$N_i \text{ (bonds per gram)} \tag{6}$$

where A represents Avogadro's number and M is the molecular weight of the basic repeating unit of the polymer. Substitution of values for N_i into eq 5 leads to

$$kI^x t = (A/M_n) - (A/M_0) \tag{7}$$

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[7] F. A. Blouin, V. J. Ott, T. Mares, and J. C. Arthur, Jr., *Textile Res. J.*, **34**, 153 (1964).

[8] F. A. Blouin and J. C. Arthur, Jr., *J. Chem. Eng. Data*, **5**, 470 (1960).

[9] F. A. Blouin and J. C. Arthur, Jr., *Textile Res. J.*, **28**, 198 (1958).

[10] C. J. Hochanadel, *Radiat. Res.*, **16**, 286 (1962).

[11] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, Inc., New York, N.Y., 1964.

[12] ASTM D-1347-56.

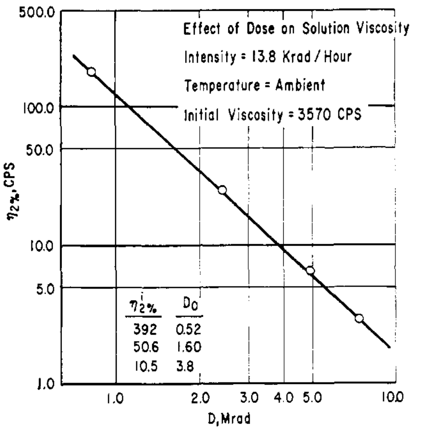

Figure 2

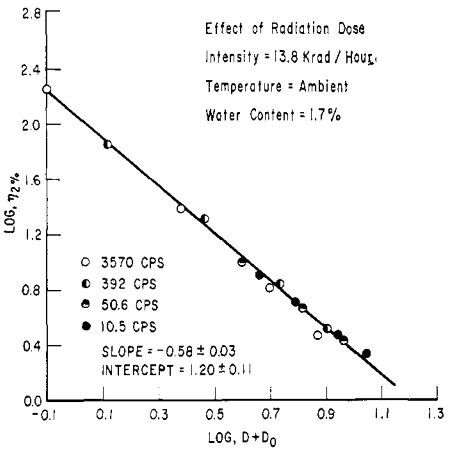

Figure 3

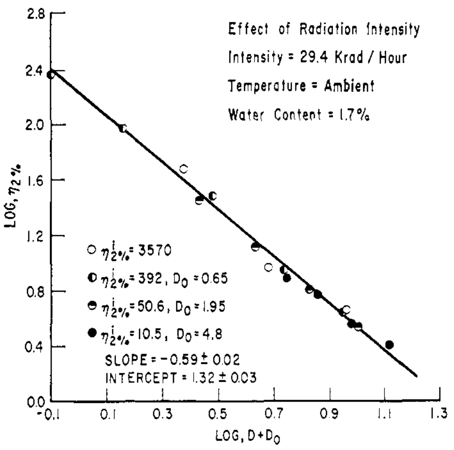

Figure 4

where M_0 is the number-average molecular weight of the polymer at the beginning of the degradation. Since the absorbed dose (D) in the polymer is defined as It, we can replace I^xt by DI^{x-1}. Further, since it can be shown that a plot of log 2% solution viscosity *vs.* log number-average molecular weight (determined by osmometry) is linear (see Figure 1), the substitution for M_n of $K\eta^\beta_{2\%}$ can be made. Substitutions into eq 7 then lead to

$$1/\eta^\beta_{2\%} = (KkDI^{x-1}A) + (K/M_0) \qquad (8)$$

which can be rearranged into the form

$$1/\eta^\beta_{2\%} = \frac{KkI^{x-1}}{A}\left(D + \frac{A}{M_0kI^{x-1}}\right) \qquad (9)$$

The last term inside the brackets has the units of molecules per bonds broken per dose, which can be interpreted as the dose (D_0) necessary to degrade a molecule of infinite molecular weight to the molecular weight defined by M_0. Making such a substitution and taking logarithms of both sides of the resulting equation

$$\log (D + D_0) = -\beta \log \eta_{2\%} + \log (A/Kk) + (1 - x) \log I \qquad (10)$$

one obtains eq 10. In the case where D is much greater than D_0, the left side of eq 10 reduces to log D. This will happen when M_0 is of a great enough value. A plot of log D *vs.* log $\eta_{2\%}$ then should yield a straight line of slope $-\beta$ and intercept log $(A/Kk) + (1 - x)$ log I. This same plot can be used to obtain fair estimates of values for D_0 for those situations in which M_0 is not large enough to satisfy the condition that $D \gg D_0$. If this is done (see Figure 2), then, by using the estimated values for D_0 and the measured values for both D and $\eta_{2\%}$, a plot of log $(D + D_0)$ *vs.* $\eta_{2\%}$ should yield a straight line, regardless of the initial molecular weight of the cellulose derivative. Such a plot is shown in Figure 3, from which it can be seen that the above kinetic model assumed to be operative for this system seems to be valid. A good fit of the data is obtained using any of the four starting 2% solution viscosities, yielding a slope of -0.58 ± 0.30 (90% confidence limits[13]) and an intercept of 1.2 ± 0.1.

If x in eq 10 is not equal to 1, then the intercept should be a function of intensity (eq 11). In order to determine the value of x, it is necessary to examine the same degradative reaction for several different intensities.

$$\text{intercept} = (1 - x) \log \text{I} + \log (A/Kk) \qquad (11)$$

This was done, and the results are shown graphically in Figures 4–6 in which the only parameter varied was the intensity, which covered the range from 13.2 to 135.8 krad/hr. The values of the intercepts, slopes and D_0 values which result from this treatment are gathered together in Table I. Examination of the last term inside the brackets of eq 9 reveals that the value for D_0 which is read from the plot of log D *vs.* log $\eta_{2\%}$ using material of high molecular weight should also be a function of the radiation intensity. This can be stated mathematically as

$$D_0 = A/(M_0kI^{x-1}) \qquad (12)$$

which leads to

$$\log (D_0) = (1 - x) \log (I) + \log (A/M_0) \qquad (13)$$

Graphical tests of eq 11 and 12 are shown in Figure 7, from which it becomes apparent that the value of x in

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[13] C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley & Sons, Inc., New York, N. Y., 1954, p 21.

TABLE I
INTENSITY RELATIONSHIPS FOR VARIOUS PARAMETERS

Intensity, krad/hr	Slope	Intercept	D_0^{392}	$D_0^{50.6}$	$D_0^{10.5}$
13.8	−0.58 ± 0.03[b]	1.20 ± 0.11	0.52	1.60	3.80
29.4	−0.59 ± 0.02	1.32 ± 0.03	0.65	1.95	4.80
72.2	−0.53 ± 0.02	1.39 ± 0.02	1.08	3.10	6.00
135.8	−0.61 ± 0.05	1.48 ± 0.08	0.85		

[a] Units are megarads. [b] 90% confidence limits.[18]

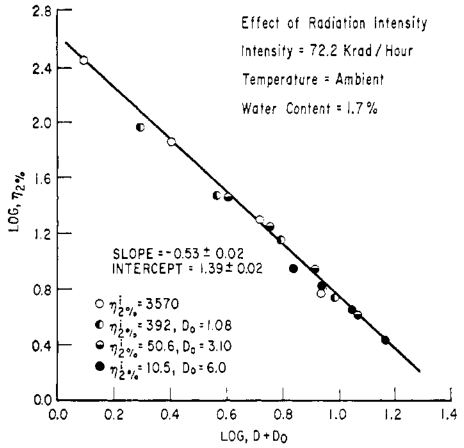

Figure 5

eq 4 is not 1. The slope of the line constructed to test eq 11 results in a value for the exponent of intensity of 0.7, a value which is probably more valid than that which is derived from the slopes of the curves constructed to test eq 13. The slopes of the lines used to test eq 13 result in values for the exponent of intensity which are not too far from the more probably correct value derived from eq 11 (average = 0.6 ± 0.1). Values for the exponent of intensity in rate equations of the order of one-half are usually interpreted in terms of a biradical termination mechanism.

Since all of the foregoing experiments were performed in the presence of both atmospheric oxygen and the equilibrium concentration of water present in the methylcellulose samples (1.7%), it was deemed necessary to examine the effects of these additives. Samples of one initial molecular weight distribution were irradiated. The pretreatment of the samples consisted of a prolonged evacuation at pressures of 3 × 10⁻⁵ mm, a technique which should effectively remove both water and oxygen from the system. The samples were irradiated in sealed ampoules after the prolonged evacuation. Treatment of the data obtained as before (see Figure 8) demonstrated quite clearly that in the absence of these two additives, the reaction proceeded at a rate which was a function of the intensity to the first power. Similar experiments, carried out under various concentrations of both oxygen and water, are summarized in Table II. Although there does seem to be some systematic trend in the values tabulated in Table II for the intercepts—within the error limits associated with these values—the numbers are identical

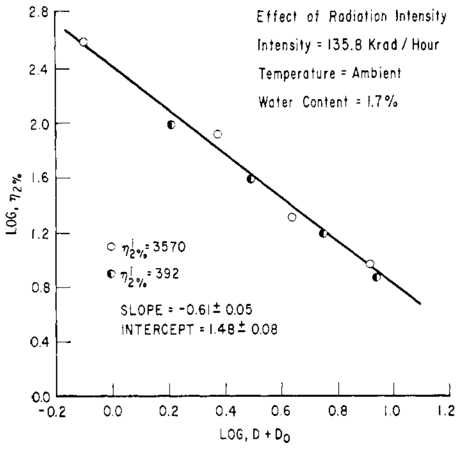

Figure 6

TABLE II
EFFECT OF AIR AND WATER[a]

Air, mm	Water, wt %	Slope	Intercept
3 × 10⁻⁵	0.0	−0.62 ± 0.04	1.66 ± 0.07
3 × 10⁻⁵	10.6	−0.64 ± 0.10	1.56 ± 0.18
748	0.0	−0.61 ± 0.03	1.61 ± 0.08
748	1.7	−0.61 ± 0.06	1.53 ± 0.11
748	10.6	−0.59 ± 0.02	1.54 ± 0.03

[a] Temperature, ambient; intensity, 149 krad/hr.

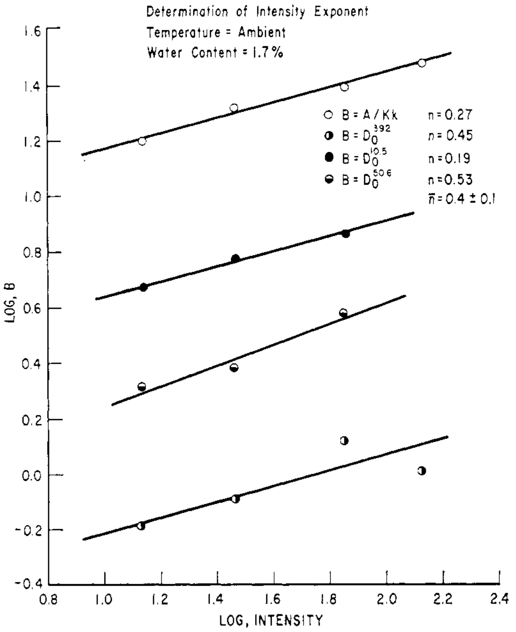

Figure 7

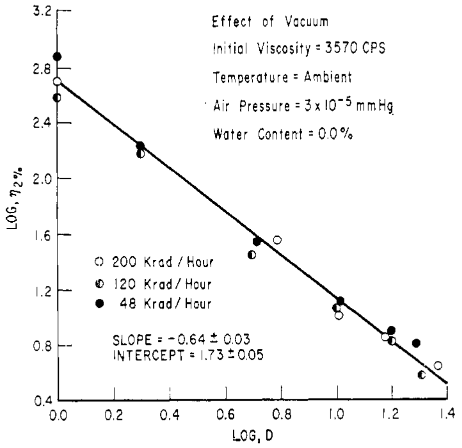

Figure 8

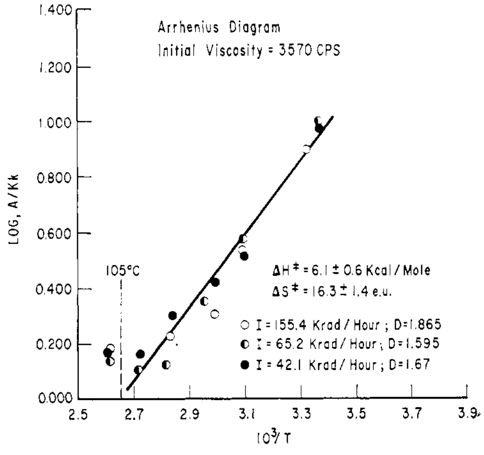

Figure 9

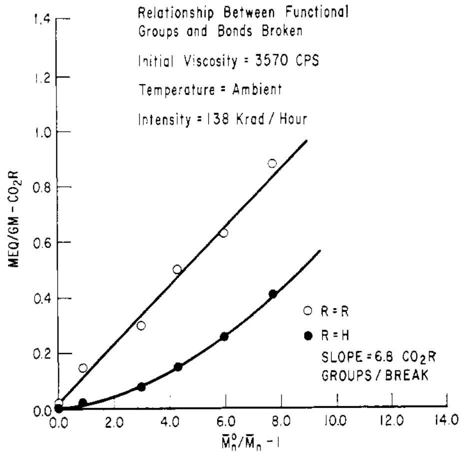

Figure 10

It was felt at this point that a convenient technique had been developed for examining the rate constant involved in the radiation–degradation of this particular methylcellulose system. In order to gain further insight into what mechanism might be operative, the determination of the activation parameters was carried out. The assumption was made for these experiments that neither the value for x nor for β was a function of temperature. The result of carrying out irradiations, analyzing the samples for 2% solution viscosity and solving for log (A/Kk) in eq 10 as a function of temperature is shown in Figure 9, along with the derived activation parameters. The values obtained are quite reasonable for a reaction involving the breaking of a unit into two subunits. The data seem to indicate a change in mechanism above about 100° which may be due to some phase change in the system.

As a further attempt to gain insight into the mechanism of this reaction, a determination of two types of functional groups which were known to be produced in the degradation reaction was carried out. A plot of the concentration of either of these two functionalities (carboxyl and carboalkoxy) as a function of the number of bonds broken per polymer molecule $(M_0/M_n - 1)$ was prepared. The result of this type of plot can be found in Figures 10 and 11. From these plots it is seen that the formation of carboalkoxy groups is a linear function of the number of chain breaks per polymer molecule, while the formation of carboxy groups is not linear with chain fracture. The number of carboalkoxy groups formed for each chain fracture can be determined from the slope of the straight lines in Figures 10 and 11 along with a knowledge of the initial molecular weight values. In both cases (Figure 10 or Figure 11), the number of carboalkoxy groups formed per chain fracture is 6.8.

As a final experiment, it was desired to know the G value for chain fracture in this particular system. Since the reaction was known to proceed at a rate which was not directly proportional to the radiation intensity, it was necessary to construct plots of bonds broken per polymer molecule $(M_0/M_n - 1)$ *vs.* total absorbed dose and extrapolate to the initial stages of the reaction. Such a plot is found in Figure 12 along with the G values for chain fracture at the initial stages of the reaction. These G values can in turn be converted into the energy involved in one chain fracture, and the values are found to be about 6.0 eV.

Consideration of the data reported here, along with the pertinent data already available in the literature, allows one to compile a list of conditions which must be satisfied in any postulated mechanism. 1. The reaction should consume oxygen. 2. The reaction should have as a first intermediate a secondary carbon radical. 3. One final product of the degradation should be an alkoxy radical. 4. The energy necessary to produce one chain fracture should be on the order of 6 eV. 5. Fractured chains should contain ester functionalities (specifically, formate ester groups). 6. The reaction should be a modest chain reaction terminating by some biradical mechanism, in the presence of air and water. 7. An intermediate in the reaction scheme should have an alternate decomposition mode leading to the formation of esters, without concurrent fracture of the chain.

The necessity for oxygen involvement in the degradation arises from the apparent oxidative character of the reaction (*i.e.*, the linear relationship between bonds broken and ester groups formed). However, since the reaction proceeds significantly even in the absence of oxygen (approximately twice as fast in the presence of oxygen, compare Figures 6 and 8), it may be that the ester products are derived from intramolecular rearrangements of some sort that occur on cleavage.

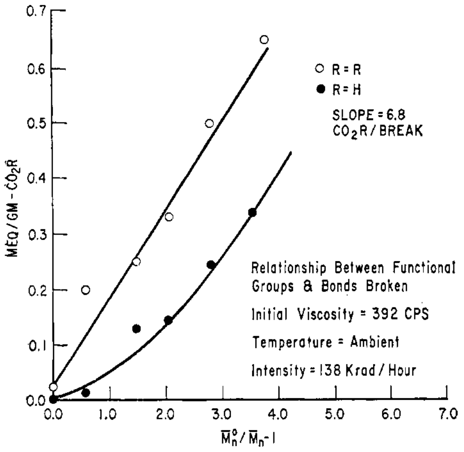

Figure 11

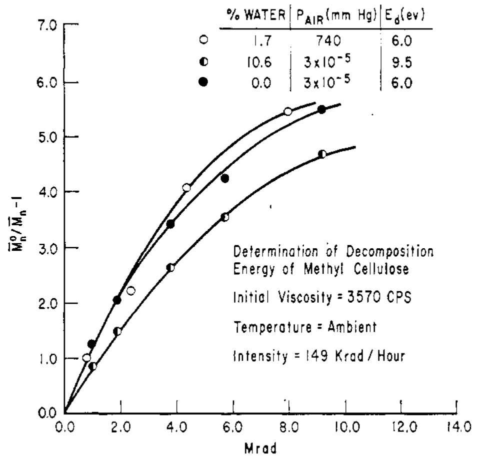

Figure 12

The initial and final radicals formed in the degradation seem to be well documented as being secondary carbon[1a] and alkoxy,[1] respectively.

Experimentally, we have found the energy necessary for chain cleavage to be approximately 6 eV. Products from the degradation of methylcellulose have been shown to be both carboxylic acids and esters[6,9] and in our work the formation of esters has been found to be linearly related to the rate of chain cleavage.

A modest chain reaction can be inferred from the difference in *G* values reported for radical formation (0.8)[1a] and that for chain fracture (16.5, Figure 12). A biradical termination mechanism can also be inferred on the basis of the experimentally determined exponent of intensity in the assumed rate law (0.7), since values of this magnitude can be best rationalized on the basis of such a termination process.

Since the number of ester functionalities formed for each chain cleavage (6.8) is not unity, there must be some common intermediate which can decompose or rearrange into an ester without the concommitant cleavage of a chain.

Although there are reaction schemes which can be postulated which account for all of the above criteria, there are not enough experimental data available on any one system to allow any firm conclusions with respect to the details of the mechanism.

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