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Chain Reaction Mechanism of Cellulose Pyrolysis

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Synopsis

Chatterjee and Conrad[1] studied the kinetics of pyrolysis of cotton cellulose in the temperature range 270–310°C and proposed a chain reaction mechanism. Lipska and Parker[8] studied the pyrolysis of the α-cellulose in the temperature range 250–300°C and interpreted the kinetic data differently. Both articles were published almost simultaneously. In this paper Lipska and Parker's complete data have been again analyzed and reinterpreted in light of the chain reaction mechanism. The energies of activation for initiation and propagation steps of the cellulose decomposition reaction are discussed.

The pyrolytic reaction of cellulose up to about 40% initial decomposition was reported to be quite complex, and the data could not be treated by any simple reaction law.[1,2] However, Tang and Neill,[3] using a dynamic TGA technique, observed a pseudo zero-order initial reaction but did not propose any mechanism to explain the fact. In previous work it had been proposed that the thermal decomposition of cellulose involved scission at the 1-4 link in cellulose followed by levoglucosan formation.[4–7] Chatterjee and Conrad[1] recently proposed an original chain reaction mechanism and considered the major reaction of cellulose as a two-step process with an initiation step as glucosidic bond scission and levoglucosan formulation as the propagation step. Thus, two equations have been derived as follows:

$$W_L = k_i k_p A_0 t^2/2 \tag{1}$$

and

$$-dW_r/dt = k_p W_r \tag{2}$$

where W_r is the residual weight of sample, W_L is the weight loss of sample, k_i and k_p are specific reaction constants for initiation and propagation reactions, respectively, and A_0 is constant. Equation (1) is applicable as long as the glucosidic bond scission is initiated, and experimentally this obtains up to about 40% of the decomposition of cellulose. Gradually, all the cellulose molecules which were initiated will transform to degraded unstable species, and the reaction will transform to a first-order type as represented by eq. (2). Tang and Neill's observation of zero-order initial reaction has been explained by assuming a stationary-state phenomenon of the reaction under dynamic heating conditions. Lipska and Parker[8] have currently published experimental results on isothermal pyrolysis of

α-cellulose, (derived from wood) in the temperature range of 250–300°C and stated that the first part of the major reaction is zero-order type. Their experimental procedure differs from that of Chatterjee and Conrad, but, in principle, both are similar since both aimed at the isothermal kinetics study of cellulose pyrolysis in the same temperature range. Therefore, in this paper Lipska and Parker's complete data have again been analyzed and are reinterpreted in light of the chain-reaction mechanism.

It has been stated that during the pyrolysis of cellulose the residual weight of the sample eventually comes to a constant value while the actual cellulose, determined by the hydrolysis method of Saeman et al.,[9] is completely lost. The constant value is obviously due to the char formation. Therefore, in the present calculation, the data[8] on pyrolysis residue have been normalized for kinetics study according to the following:

$$W_r = [(W - W_\infty)/(W_0 - W_\infty)] \times 100$$

where W_∞ is char content (per cent), W is pyrolysis residue, and W_0 is initial amount of cellulose (100%). This method of normalization of the data is slightly different from that followed by Lipska and Parker. They simply subtracted W_∞ from W to obtain W_r.

A first-order reaction plot with respect to pyrolysis residue (W_r) showed deviations up to about 40–50% initial decomposition of cellulose, as was also reported by Lipska and Parker and others.[1,2] A similar deviation in the initial part is observed in a first-order plot with respect to cellulose (remaining anhydroglucose units).

Now, according to the chain-reaction mechanism, slopes of the straight-line portions (0–60%) in first-order plots give the rate constants k_p of the propagation step for the decomposition of cellulose. The kinetic run at 250°C was not continued far enough to obtain the second stage of reaction[8] and, therefore, k_p values could not be determined.

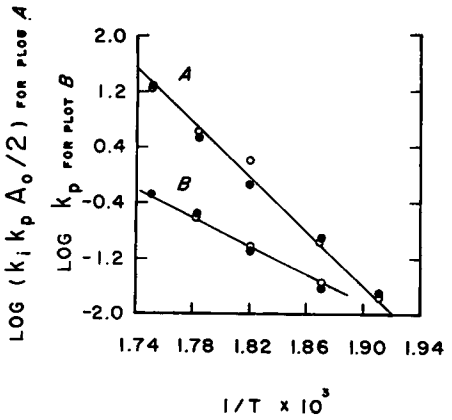

Fig. 1. Determination of the energies of activation for the initiation and propagation steps: (●) weight loss data and (○) cellulose loss data for (A) first stage of pyrolysis; (B) second stage of pyrolysis.

The Arrhenius plot of the propagation reaction is shown in Figure 1 (plot B). Both series of data fall on a single straight line, giving an energy of activation E_p = 42 kcal/mole. The value is the same as that found by Lipska et al. It may now be considered that all reported values of energies of activation which were calculated from a first-order plot of the second stage of reaction are the activation energies for only the propagation step of cellulose decomposition. Hence, in Table I, the literature values of E_p have been compared.

TABLE I
Energy of Activation for Propagation Step of Cellulose Pyrolytic Reactions

Sample	Temperature range, °C	E_p, kcal/mole	Reference
Absorbent cotton	270–310	33.0	1
Ball-milled cotton cellulose	275–300	37.1	1
Cotton cellulose	Above 250	33 ± 3	4
α-Cellulose	100–250	34–39.4	10
Cotton cellulose	275–300	50	2
α-Cellulose (Whatman grade 1 chromatographic paper)	240–310	53–56	3
α-Cellulose (from wood)	250–298	42	8 and present calculation

The high value of energy of activation reported by Madorsky et al. (50 kcal/mole) is probably due to the fact that their calculation is based on weight loss rates taken near the middle of the pyrolysis range without taking char formation into account.[8] Tang and Neill[3] also obtained a high value (53–56 kcal/mole) by the dynamic TGA method. However, the procedure for the treatment of the data, which Tang and Neill followed, may not be adequate for cellulose pyrolytic reactions due to the complicated reaction mechanism. The limitations of the above method have been discussed recently.[11]

Figures 2 and 3 show the representation of eq. (2) with the present data for initial stage of the reaction. In Figure 2, W_L represents the weight loss of sample $(100 - W_r)$ and in Figure 3, C_L represents the loss of cellulose or glucosan units $(100 - C_r)$. The validity of the chain-reaction mechanism has been confirmed by the linearity of plots. However, none of the straight lines pass through the origin. Since the information regarding the initial time-lag effect, inherent in the experimental technique, is lacking, it is, therefore, difficult to explain the cause of such discrepancies. If it is not due to the experimental limitation then one could infer that an extremely rapid reaction takes place at the very early stage of the initial reaction, which accounts for about 6–10% of the total reaction.

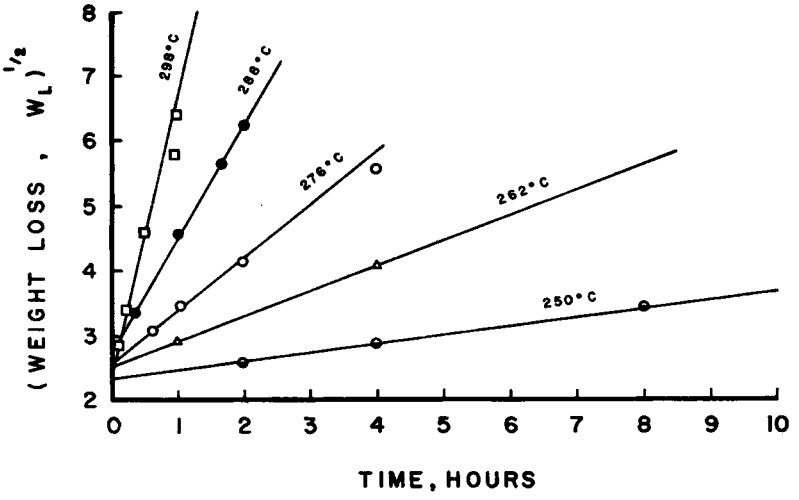

Fig. 2. Square-root relationship between weight loss W_L during the initial stage of pyrolysis and time.

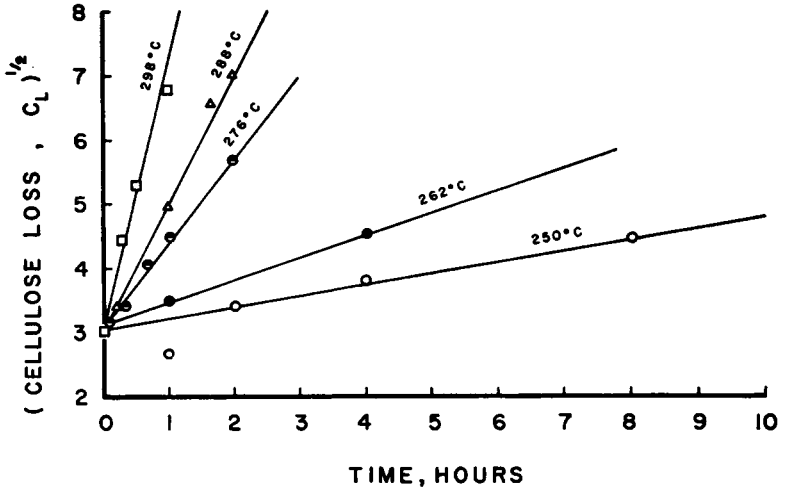

Fig. 3. Square-root relationship between loss of cellulose (glucosan units) C_L during the initial stage of pyrolysis and time.

According to eq. (2), the slope of the straight lines in Figures 2 and 3 give values of $[k_t k_p A_0/2]^{1/2}$, where A_0 is independent of temperature. Considering the Arrhenius equation, the following expression can be derived:

$$\log k_t k_p(A_0/2) = (1/2.303RT)\cdot(E_t + E_p) + \log [Z_t Z_p A_0/2] \quad (3)$$

A plot of $\log [k_t k_p(A_0/2)]$ against $1/T$ is shown in Figure 1 (plot A). Again both series of points fall along the same straight line. The sum of energies of activations $(E_t + E_p)$ have been calculated from the slope of the straight

TABLE II
Kinetics of the Pyrolysis of α-Cellulose

Temperature, °C	Reaction constants from loss of cellulose data				Reaction constants from weight loss data			
	k_p	$k_i k_p A_0/2$	E_i, kcal/mole	E_p, kcal/mole	k_p	$k_i k_p A_0/2$	E_i, kcal/mole	E_p, kcal/mole
250	—	0.0177			—	0.0204		
262	0.0295	0.1184			0.0233	0.1498		
276	0.0993	1.675	49	42	0.0800	0.6988	49	42
288	0.2667	3.887			0.2972	3.016		
298	—	17.26			0.5272	18.26		

line. By subtracting E_p from the sum, the energy of activation for the initiation reaction has been calculated. The results are tabulated in Table II.

The energy of activation for the initiation of the pyrolysis of cotton cellulose[1] was found to be 54 kcal/mole. The value in this case is lower by 5 kcal. At this stage, it is difficult to explain why the activation energy for the propagation reaction is slightly higher and for the initiation reaction it is slightly lower than those in the case of cotton cellulose. This difference may arise from the morphological or structural differences in fibers or it may be due to the difference in the level of impurities such as hemicellulose, etc., which are thermally more unstable.[12] It could also be due to the difference in experimental techniques.

It is concluded that the kinetics of the chain reaction mechanism are also consistent with the experimental results on the pyrolysis of α-cellulose, published by Lipska and Parker.[8] One more important factor is that the kinetics of pyrolytic reaction would reveal essentially the same fact whether it is followed by simple weight loss measurement or by the measurement of the loss of cellulose by analytical methods, provided the former data are normalized properly by taking into account the percentage of char formation.

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