Theory of Thermal Decomposition and Volatilization of Normal Alkanes and Linear Polyethylene

1. Random Decomposition and Volatilization at Constant or Variable Temperature

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SUMMARY

The fragmentation of linear polyethylene of high molecular weight, of normal alkanes, and of other nonbranched poly- α- olefins in a pyrolyzer connected with a gas chromatograph was studied previously. From the evaluation of the fragments longer than C_{11} or than the respective pentamers a random decomposition process was suggested for these polymers. This process was described with characteristic cleavage probabilities for the C-C-bonds in the backbone of the chain. It is not possible to apply this simple model to the decomposition of normal alkanes without consideration of the volatilization. An approach to this problem is presented in this paper.

INTRODUCTION

In the previous paper [1] the thermal decomposition and volatilization from a pyrolyzer employed in the analysis of the primary structure of polymers was studied. To measure the effect of chain length upon degradation and volatilization, the normal alkenes n- C_{18}, n- C_{24}, n- C_{32} and n- C_{40} were subjected to pyrolysis. The fragment distributions demonstrate very clearly a convergence to the fragment distribution of linear polyethylene of high molecular weight, when the chain length of the normal alkane is increased.

Fragments have also been detected up to the range of C_{55}- C_{60} from pyrolyses of high molecular polyisobutylene and polypropylene. It has been shown that this limit is not characteristic for the mechanisms of decomposition and volatilization, but is merely symptomatic of absorption processes in the flow system for carrying the fragments through a gas chromatograph. These effects of absorption, which were suppressed for fragments less than C_{45}, are not a subject of this present study.

In contrast to the poly- α- olefins with a whole spectrum of fragments there are many polymers which decompose by unzipping to monomers [2]. It can be considered that the short fragments are readily volatilized after their generation [3]. Also, in such polymers the volatilization is not the rate determining step in the whole degradation. However, if there is a great difference in the vapor pressure of the various fragments, the simultaneous volatilization has to be considered in addition to the thermal decomposition.

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For linear polyethylene a theory of random cleavages and of volatilization at a constant temperature was established by SIMHA and WALL [4]. With 2x as the chain length of the original polymer a set of 2x coupled differential equations must be solved. Since 2x may be very large, an approach was made by introducing a critical chain length L to separate the region of pure degradation above L from that of degradation and volatilization as well. This approach is also usefull to discriminate the the pyrolysis of high molecular weight polymers (long chains) from the pyrolysis of oligomers (short chains). A further simplification was made by neglecting the combination of fragments. There was no direct evidence of this, but recent pyrograms of normal alkanes have shown that fragments longer than the initial chain length 2x are indeed negligible [1].

The theory of SIMHA and WALL will be discussed in more detail in Section II. The experimental setup used in their study was rather simple: An evacuated system with a furnace surrounding the polymer, and a cold trap for the collection of the volatilized fragments. It was only possible to obtain average values for the molecular weight distribution in the trap. Thus, little emphasis was put on the direct course of the fragment distribution.

Basically the same model can be applied to the present day pyrolyzer and gas chromatograph: The pyrolyzer is the furnace and the g. c. separation column corresponds to the trap. However the column is a more sophisticated tool to determine the distribution of the volatile decomposition products.

Since polyethylene (PE) has been most extensively studied among poly- α-olefins [5] it was choosen to demonstrate the distribution of the volatile decomposition products. This application of the theory will be presented in a following paper.

THEORY - I. RANDOM DECOMPOSITION, WITHOUT VOLATILIZATION

According to a calculation first made by W. KUHN [6] for linear polymers, the fragment distribution follows from

$$\tilde{N}_c = M \cdot s_o^2 \cdot (1 - s_o)^{c-1} \qquad (1)$$

where $\tilde{N}_c$ is the number of fragments with length c in the polymer $(1 \leqq c \leqq 2x)$. It is considered here, that the length of the polymer chain 2x is very large compared to the length c of the fragments.

$M = \sum_c \tilde{N} \cdot c$ is the number of all carbon atoms present in the fragments. This number is approximately proportional to the initial weight of polymer. s_o denotes the cleavage probability for a C–C- bond $(0 \leqq s_o \leqq 1)$.

For short chains with a finite length 2x one obtains in a similar way [7]

$$\tilde{N}_c = s_o \cdot (1 - s_o)^{c-1} \cdot [2 + s_o (2x -1 -c)] \cdot M/ 2x , \quad c < 2x \qquad (2)$$

$$\tilde{N}_c = (1 - s_o)^{2x-1} \cdot M/ 2x \qquad . \qquad (3)$$

Calculations with these equations were originally made to study the random decomposition of cellulose.

Apart from a normalizing factor, Eq. (1) was found to desribe properly the distribution of volatilized fragments larger than C_{11} from linear polyethylene of high molecular weight. With s as the cleavage probability, the distribution was proportional to $(1-s)^{c-1}$. Thus, it was concluded that a random decomposition process occurs [8]. The same was found to be the case in other poly- α- olefins [9].

However, in the studies the effect of volatilization was not considered, which is why it is not possible to fit Eqs. (2) and (3)to the measured fragment distribution of normal alkanes [1, 8]. The reason for this discrepancy is clear, since the measured distribution is that of volatilized fragments and not of the fragments of the residue. Thus, what has been proven as a good model to describe the degradation of high molecular weight polymers fails when applied to short chains or oligomers.

II. RANDOM DECOMPOSITION AND VOLATILIZATION AT CONSTANT TEMPERATURE

The first order kinetic equations given by SIMHA and WALL [4] for an open system with a random decomposition and volatilization of the products are rewritten in this paper in the following form

$$\frac{d \tilde{N}_c(t)}{dt} = 2k \left(\sum_{z=1}^{z=2x-c} \tilde{N}_{c+z}(t) \right) - k \cdot (c-1) \cdot \tilde{N}_c(t) - p_c \cdot \tilde{N}_c(t) \quad (4)$$

$$\frac{d N_c(t)}{dt} = p_c \cdot \tilde{N}_c(t) \quad (5)$$

$\tilde{N}_c(t)$ and $\tilde{N}_{c+z}(t)$ denote the number of molecules at time t with length $c \leq c+z \leq 2x$ in the polymer residue, $N_c(t)$ is the number of molecules vaporized. $2x$ is the chain length of the originally monodisperse polymer. k is the rate constant for splitting a C-C bond in any of the $\tilde{N}_c(t)$ molecules and is - a random cleavage is assumed - independent of c, $c+z$ or of the position of the link, and p_c represents the rate constant for the evaporation of the $\tilde{N}_c$ molecules in the residue.

With time constants k and p_c Eq. (4) has the following solution

$$\tilde{N}_c(t) = \sum_{r=0}^{r=2x-c} H_{c+r,c} \cdot \exp(\lambda_{c+r} \cdot t) \quad (6)$$

$$\lambda_{c+r} = - ((c+r-1) \cdot k + p_{c+r}) \quad ; \quad 0 \leq r \leq 2x-c \quad (7)$$

The coefficients $H_{c+r,c}$ are determined for $r \neq 0$ from the characteristic equation

$$H_{c+r,c} = \frac{2k}{\lambda_{c+r} - \lambda_c} \cdot \left(\sum_{z=1}^{r} H_{c+r,c+z} \right) \quad ; \quad \lambda_{c+r} \neq \lambda_c \quad (8)$$

The diagonal elements H_{cc} of the triangular matrix H are derived from the boundary condition at $t = 0$ $(c < 2x)$

$$\tilde{N}_c(0) = 0 \quad (9)$$

$$H_{cc} = - \sum_{r=1}^{2x-c} H_{c+r,c} \quad (10) \qquad H_{2x,2x} = \tilde{N}_{2x}(0) \quad (11)$$

where $\tilde{N}_{2x}(0)$ is the initial number of polymer chains. With Eqs. (8), (10) and (11) all the $x(2x+1)$ elements of the matrix H can be calculated.

The number of molecules which are volatilized at time t follows from integration of Eq. (5)

$$N_c(t) = \int_0^t p_c \cdot \tilde{N}_c(t') \, dt' \quad (12)$$

If a complete volatilization of all polymer at a constant temperature is considered for $t \to \infty$, then Eq. (12) approaches

$$N_c = p_c \cdot (\sum_{r=0}^{2x-c} \frac{H_{c+r,c}}{-\lambda_{c+r}}) \qquad ; \qquad N_c = N_c \ (t=\infty) \quad . \qquad (13)$$

A. Long Chains [4]

If $2x$ is very large, a critical chain length L can be introduced with $p_c = 0$ for $c \geqq L$. In this region $(L \leqq c \leqq 2x)$ only random scission occurs and no volatilization. Then from Eq. (8) follows that

$$H_{cc} = (2x-c+1) \cdot \tilde{N}_{2x}(0) \quad (14) \qquad H_{c+1,c} = -2 \cdot (2x-c) \cdot \tilde{N}_{2x}(0) \quad (15)$$

$$H_{c+2,c} = (2x-c-1) \cdot \tilde{N}_{2x}(0) \quad (16) \qquad H_{c+r,c} = 0 \ , \quad \text{for } r \geqq 3 \ .$$

The transition $2x \to \infty$ can be made with the finite initial weight of polymer $M = 2x \cdot \tilde{N}_{2x}(0)$.

Usually the kinetic equations are checked with the number average chain length, which is defined as

$$\overline{c_n}(t) = \sum_{c=1}^{2x} c \cdot \tilde{N}_c / \sum_{c=1}^{2x} \tilde{N}_c \qquad . \qquad (17)$$

If the amount of volatilizable fragments $\tilde{N}_c(t)$ with $c < L$ can be neglected, then from Eq. (6)

$$1 / \overline{c_n}(t) = s_0 + (1-s_0) / 2x \qquad . \qquad (18)$$

Here, as in section I, s_0 is the fraction of bonds which have been cleaved. The calculation yields the same equations for $\tilde{N}_c(t)$ as Eqs. (1) - (3), when s_0 is written as

$$s_0 = 1 - e^{-kt} \quad . \qquad (19)$$

To calculate the distribution of the volatilized fragments N_c , the following approximation in Eq. (8) can be made

$$H_{c+r,c} = -2k \cdot H_{c+r,c+r} / (p_{c+r} - p_c) \ , \quad \text{for } c \text{ and } c+r<L \ . \ (20)$$

Eq. (20) is also valid for $c+r=L$ and $c+r=L+1$ if p_{c+r} is cancelled in the denominator. For all $c+r>L+1$ $H_{c+r,c} = 0$.
Then Eq. (13) yields with $M = 2x \cdot \tilde{N}_{2x}(0)$:

$$N_c = \frac{2M}{(L-1)L} \ , \quad \text{for } c<L \ , \quad L \leqq 2x \qquad . \qquad (21)$$

This result - that N_c becomes approximately independent of the fragment length c and of 2x - has already been discussed by SIMHA and WALL [4]. It was used for an estimation of L, which was reported as L = 72 for linear polyethylene.

B. Short Chains

For $2x < L$, p_{2x} is not negligible compared to $k(2x-1)$. The parent peak N_{2x} can be measured then. From Eq. (11) and Eq. (13) - with $c=2x$ and $r=0$ - follows

$$N_{2x} = \tilde{N}_{2x}(0) \cdot \frac{p_{2x}}{(2x-1) \cdot k + p_{2x}} \qquad (22)$$

$N_{2x}/\tilde{N}_{2x}(0)$ is the fraction of polymer volatilized without decomposition. The distribution of the fragments with $c<2x$ can be calculated in the same

way from Eq. (13) with the approximation in Eq. (20)

$$N_c = \tilde{N}_{2x}(0) \cdot \frac{2 \cdot k}{P_{2x}} \qquad , \qquad c < 2x \quad . \tag{23}$$

N_c becomes independent also of c, as in Eq. (21).

III. RANDOM DECOMPOSITION AND VOLATILIZATION AT VARIABLE TEMPERATURE

From the temperature risetime measurements reported previously [1] it was obvious that a constant temperature is not the general case in pyrolysis experiments. Since k and p_c are functions of the temperature, they are also functions of time in the case of a variable temperature. In this section the influence of the finite risetime of the temperature is discussed in paticular.

A. Long Chains

With the assumptions made in the preceding section for c above the critical length L Eq. (4) is replaced by

$$\frac{d \tilde{N}_c(t)}{dt} = 2k(t) \cdot (\sum_{z=1}^{2x-c} \tilde{N}_{c+z}(t)) - k(t) \cdot (c-1) \cdot \tilde{N}_c(t) \quad . \tag{24}$$

For this equation the solution may be written as

$$\tilde{N}_c(t) = \sum_{r=0}^{2x-c} H_{c+r,c}(t) \cdot \exp(\lambda_{c+r}(t) \cdot t) \tag{25}$$

$$\lambda_{c+r}(t) = - (c+r-1) \cdot k(t) \qquad . \tag{26}$$

Combination with Eq. (24) yields a differential equation

$$\dot{H}_{c+r,c}(t) + H_{c+r,c}(t) \{\lambda_{c+r}(t) - \lambda_c(t) + \dot{\lambda}_{c+r}(t) \cdot t\}$$
$$= 2k(t) \cdot \sum_{z=1}^{r} H_{c+r,c+z}(t) \quad . \tag{27}$$

$\dot{H}_{c+r,c}(t)$ and $\dot{\lambda}_{c+r}(t)$ are the respective first order derivatives.
In addition to the boundary conditions in the Eqs. (9) and (11) the solution should also be convergent to Eqs. (14) – (16) if k becomes a constant of time. This simplifies the finding of the solution of Eq. (27), which is for $c \gtreqless L$

$$H_{cc}(t) = (2x-c+1) \cdot \tilde{N}_{2x}(0) \cdot \exp ((c-1) \cdot I_k(t)) \tag{28}$$

$$H_{c+1,c}(t) = - 2 \cdot (2x-c) \cdot \tilde{N}_{2x}(0) \cdot \exp (c \cdot I_k(t)) \tag{29}$$

$$H_{c+2,c}(t) = (2x-c-1) \cdot \tilde{N}_{2x}(0) \cdot \exp ((c+1) \cdot I_k(t)) \tag{30}$$

$$H_{c+r,c}(t) = 0 \quad , \quad \text{for} \quad r > 2 \quad (c+r \leqq 2x) \quad . \tag{31}$$

Here the function $I_k(t)$ is the integral

$$I_k(t) = \int_0^t (dk/dt') \cdot t' \, dt' \tag{32}$$

which has a zero value for $t = 0$ as well as for $(dk/dt') = 0$, in cor-

respondence with the boundary conditions.

Thus, for $\tilde{N}_c(t)$ in Eq. (25) follows $(L \leqq c < 2x)$:

$$\tilde{N}_c(t) / \tilde{N}_c(O) = (2x-c+1) \cdot \exp\{(c-1) \cdot (I_k(t) - k(t) \cdot t)\} - 2 \cdot (2x-c)$$
$$\cdot \exp\{c \cdot (I_k(t) - k(t) \cdot t)\} + (2x-c-1) \cdot \exp\{(c+1) \cdot (I_k(t) - k(t) \cdot t)\} \tag{33}$$

The result for $\tilde{N}_{2x}(t)$ is

$$\tilde{N}_{2x}(t) / \tilde{N}_{2x}(O) = \exp\{(2x-1) \cdot (I_k(t) - k(t) \cdot t)\} \tag{34}$$

The calculation of the average fragment length $\overline{c}_n(t)$ according to Eq.(17) leads to the same expression as in Eq. (18), when one writes for the fraction of cleaved bonds in the considered case

$$s_o = 1 - \exp (I_k(t) - k(t) \cdot t) \tag{35}$$

Thus, the problem of finding the distribution of fragments with L and larger is reduced to the calculation of the integral in Eq. (32).

As an example, a linear temperature rise is assumed. Some authors [5] have determined this experimentally under controlled conditions. With T_o as the temperature at start $(t=O)$ and $\xi = dT/dt$ as the constant heating rate, the time can be transformed into the temperature

$$t = (T-T_o)/ \xi \quad , \quad (O \leqq t \leqq t_1 ; \quad t_1 = \text{temperature rise time}) . \tag{36}$$

An ARRHENIUS equation might be assumed for $k(t)$ as a function of the temperature

$$k(T) = k_o \cdot \exp -(\Delta E_k/ RT) \quad , \tag{37}$$

where k_o is a constant, ΔE_k the activation energy for random chain cleavage (cal/ mole), and $R \simeq 2$ cal/ mole ^oK (the gas constant).

It is convenient to introduce the dimensionless variable $w = \Delta E_k/ RT$. Then Eq. (32) becomes with Eq. (37)

$$I_k(t) = \frac{k_o \cdot \Delta E_k}{\xi \cdot R} \cdot \{ \int_{w_o}^{w} dw' \, (1 - \frac{w'}{w_o}) \cdot e^{-w'} \cdot \frac{1}{w'} \} \quad , \tag{38}$$

where $w_o = \Delta E_k/ RT_o$ $(t=O)$, and w is calculated at time t . This function $I_k(t)$ is related to the exponential integral

$$E_1(\omega) = \int_{\omega}^{\infty} d\omega' \, \frac{e^{-\omega'}}{\omega'} \quad , \quad \text{which has been tabulated} [10, 11] .$$

It is not necessary to use the tables when w and w_o are large. The activation energy for chain cleavage in linear PE was reported to be about 70 kcal/ mole [2] . For temperatures $T<1000$ ^oK RT is less 2 cal/ mole. Consequently w retains values greater than 35. In Eq. (38) integration by parts and expansion into a series is possible, where terms of higher order than $(1/w)^2$ are negligible. The product $k(t) \cdot t$ can be transformed into a similar expression.

At time t and the temperature T one obtains

$$I_k(t) - k(t) \cdot t \simeq - \frac{R \cdot t}{\Delta E_k \, (T-T_o)} \cdot (T^2 \cdot k(T) - T_o^2 \cdot k(T_o)) \quad . \tag{39}$$

It is then possible to calculate the distribution in Eq. (33) and Eq. (34) as well as s_o in Eq. (35).

We use this result to calculate the average fragment length in the residue according to Eqs. (18) and (35) at the end of the temperature rise $t_1 = (T_1-T_o)/\xi$, when the temperature is T_1 . To simplify the calculations, the following assumptions are made:

1) The chain length of the polymer at start was infinite, i.e. $2x \to \infty$ at $t=0$,

2) no pyrolysis occurs at the temperatute T_o , or $k(T_o) \ll k(T_1)$,

3) $1/\overline{c_n}(t_1) \ll 1$.

The last assumption makes it possible to expand the exponential function in Eq. (35) into a series, which leads in a first (linear) approximation to the expression

$$1/\overline{c_n}(t_1) \stackrel{\backsim}{=} (\frac{R \cdot T_1}{\Delta E_k}) \cdot (\frac{T_1}{T_1-T_o}) \cdot t_1 \cdot k(T_1) \qquad . \qquad (40)$$

It is now assumed that for $t \geq t_1$ pyrolysis occurs under isothermal conditions with the temperature T_1 . For the number average chain length corresponding to Eqs. (18) and (19) follows at time $t_2 > t_1$

$$1/\overline{c_n}(t_2) = s_o + (1-s_o)/\overline{c_n}(t_1) \qquad (41)$$

$$s_o = 1 - \exp -(k(T_1) \cdot (t_2-t_1)) \qquad . \qquad (42)$$

The pyrolysis time t_2 used in this expression is defined by $\overline{c_n}(t_2) = L$ ($L \gg 1$). At this time t_2 the fragments in the residue are volatilizable and do not decompose further.

It is reasonable to consider the temperature risetime t_1 as shorter than the time interval (t_2-t_1) , where the pyrolysis occurs under isothermal conditions until the fragments have reached the size of about L. From the reported temperature risetime measurements [1] it is obvious that this assumption can be made if the final temperature is not very high. For $t_1 < (t_2-t_1)$ the combination of Eqs. (41) and (42) with (40) yields

$$\overline{c_n}(t_1) / \overline{c_n}(t_2) > (\frac{\Delta E_k}{RT_1}) \cdot (T_1- T_o)/ T_1 \qquad . \qquad (43)$$

Since $\Delta E_k \gg RT_1$, the average chain length at t_1 is considerably greater than L (equal $\overline{c_n}(t_2)$) introduced as the upper limit for the volatilization. Under these conditions the finite risetime t_1 should have no effect on the yield and the distribution of volatiles with $c<L$.

B. Short Chains

For chains with $2x < L$ the time dependent volatilization has to be considered too . This can be done by introducing $k(t)$ as well as $p_c(t)$ into the general differential equations (4) and (5). The solution $N_c(t)$ can be written in the same form as Eq. (25) with $H_{c+r,c}(t)$ as functions of time. This method is known as the variation of the constant.

It is interesting to know for the "parent peak" $2x$ how much has been volatilized during the temperature rise. The solution of Eq. (4) ($c=2x$) is

$$\overset{\backsim}{N}_{2x}(t) = H_{2x,2x}(t) \cdot \exp(\lambda_{2x}(t) \cdot t) \qquad (44)$$

$$\lambda_{2x}(t) = - (2x-1) \cdot k(t) - p_{2x}(t) \qquad \qquad . \quad (45)$$

This equation (44) leads to a differential equation for $H_{2x,2x}(t)$, which has the following solution

$$H_{2x,2x}(t) = H_{2x,2x}(0) \cdot \exp(\int_{o}^{t} dt' t' \{(2x-1) \frac{dk}{dt'} + \frac{dp_{2x}}{dt'} \}) \quad . \quad (46)$$

Thus, the amount of normal alkane nC_{2x} present in the pyrolyzer after time t from start is

$$(47)$$

$$\tilde{N}_{2x}(t) = \tilde{N}_{2x}(0) \cdot \exp\{(2x-1)(I_k(t) - k(t)\cdot t) + I_{p2x}(t) - p_{2x}(t)\cdot t\}.$$

$I_k(t)$ was defined through Eq. (32). Similarly it is

$$I_{p2x}(t) = \int_{o}^{t} (dp_{2x}/ dt') \cdot t' dt' \qquad \qquad . \quad (48)$$

To calculate the integral (48) the same procedure can be applied as with the integral $I_k(t)$. For the rate of evaporation, an exponential relationship with $2x$ can be assumed. This might be written in the following form

$$p_{2x}(T) = p_e \cdot \exp - (2x\cdot\Delta E_p/RT) \qquad \qquad (49)$$

with p_e as a constant (from extrapolation $2x \to 0$ or $T \to \infty$). ΔE_p may be correlated to the cohesive energy of one $-CH_2-$ group. For a polyethylene in the liquid phase reported values are about 1 kcal/ mole $-CH_2-$ [12]. Even for small chains the linearity between the cohesive energy of the chain and the chainlength has been proven as a good approximation.

The integration can be carried out with $2x\cdot\Delta E_p/RT$ as a variable. If $2x$ is not too small, this variable also retains large values. Consequently the same kind of approximations as in the previous section (A) can be applied here. If volatilization at T_o is neglected $(p_{2x}(T_o) \ll p_{2x}(T_1))$ as well as decomposition during the temperature rise $(k(T) \ll p_{2x}(T))$ for $T < T_1$, it follows

$$\tilde{N}_{2x}(t_1) / \tilde{N}_{2x}(0) \simeq \exp - \{\frac{RT_1}{2x\cdot\Delta E_p} \cdot \frac{T_1}{T_1 - T_o} \cdot t_1 \cdot p_{2x}(T_1)\} \qquad . \quad (50)$$

This equation describes the fraction of normal alkane which has not been volatilized before the temperature has reached the final value T_1 . This function varies strongly with $2x$ and converges rapidly to unity when $2x$ is increased.

An application of this theory will be presented in a following paper.

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