

Pyrolysis Kinetics of a Western High Volatile Coal

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Although a number of time studies have been made on coal devolatilization, three principal models have been developed to explain the weight loss curves (1).

This study is an attempt to evaluate the mechanism of pyrolysis of a Western U. S. high volatile coal. The weight loss-time curves are interpreted according to the three classical models and as a simple unimolecular reaction. A new mechanism, more in accord with all the data, is proposed.

Several typical pyrolysis curves are plotted in Figure 1. In each instance the weighed coal sample was placed on a quartz spring, thermogravimetric furnace and the weight loss determined as a function of time. In the figure the ordinate is the fractional weight loss $\Delta W/W_0$. In the equations that follow, the following definitions apply. W_0 = initial sample weight on an ash free basis. $x = [W/W_0]$. $a = [W/W_0]_{\max}$ (at infinite time). $Z = x/a$. ΔH^\ddagger = heat of activation. ΔS^\ddagger = entropy of activation. E = activation energy (Arrhenius). R^\cdot is a reactive intermediate similar to van Krevelen's metaplast. B_i is the initial concentration of the i th species in Pitt's pyrolysis mechanism.

The general differential equation defining an n th order reaction is $dx/dt = k(a-x)^n$ when k is the reaction rate constant: In a graph of $\log(dx/dt)$ vs $\log(a-x)$, the slope of the line gives the value of n . In Figure 2, it is noted that the apparent order of the reaction varies from an initial 4.5 to unity. Obviously the decomposition is not by a simple unimolecular mechanism.

Earlier writers on coal pyrolysis kinetics (2-9) have assumed the basic reaction to be at least one unimolecular decomposition followed by other slower steps which become rate determining. Intuitively (10) bond breaking reactions of organic molecules would be unimolecular and the reaction rate proportional to the remaining undecomposed volatile producing material $(a-x)$. To determine whether a region of "first order" kinetics exists the $\log(1-x/a)$ can be plotted versus time as in Figure 4. All of the curves are linear for the first 10-15 minutes and for times in excess of 200 minutes. If it is assumed that one or the other linear portion of the curve represents true first order rate dependence the slope of the line k_i (initial) or k_f (final) would be the rate constant.

The validity of the assumption can be checked by determining the magnitude of the heat and entropy of activation from Arrhenius or Eyring Absolute Reaction Rate plots of the log of the rate versus $1/T$. Figure 5 is an Arrhenius plot of k_f (fit by least squares). The activation energy is 2.4 kcal/mole. This value is considerably less than Pitzer's (11) value of 80 kcal for C-C bond decomposition. The entropy of activation which should be almost zero, is -50 e.u.

Arbitrarily selected times of 150 and 500 minutes were chosen to determine rate constants in Figure 6. The values of "a" determined by extrapolation to infinite time were less than the experimental values in all cases.

Arrhenius plots of the rate constants (Fig. 7) and Eyring plots, fit by the method of least squares give $E = 10.6$ kcal/mole and $\Delta H^\ddagger = 9$ kcal/mole respectively.

To a large extent the volatile matter is released from the coal during the first 10 to 30 minutes. The initial rate constants should be the most significant. The least square Arrhenius plot (Fig. 8) gives activation energy of 26.6 kcal/mole. The ΔH^\ddagger is 24.8 kcal/mole and the entropy of activation is -10.1 e.u.

It has been suggested by Reed (12) that the intercept at infinite temperature of an activation energy plot may be a more reliable test of a unimolecular mechanism than the activation energy. Daniels (13) states that for most unimolecular bond breaking reactions the entropy of activation in an Eyring plot is almost zero since the activated complex is so much like the original reactants. This means that the frequency factor from an Arrhenius plot should be $\sim 10^{13}$. In each region of coal decomposition, initial, intermediate, or final it is seen that energy considerations rule out simple unimolecular decomposition as being rate determining.

Since a simple unimolecular kinetic model does not explain the weight loss curve, or even parts of it rigorously, three extensions have been advanced. The first of these might be roughly defined as the unimolecular approach. This assumes that the weight loss-time curve can be defined by a number of independent unimolecular decompositions. Various writers (2-5) have considered from one to five, although Pitt (6) derives the general case where a great many decompositions take part in the weight loss curve.

The second model was proposed by N. Berkowitz (7). In his representation, he assumes as coal is placed in a hot environment, that a rapid pyrolytic reaction occurs. This reaction produces a large volume of volatile material that is stuffed into the inter-porous space of the coal particle. He postulates a slow diffusion of volatile matter from the inter-porous volume as giving rise to the kinetics. He considers the initial decomposition as unimolecular and estimates appropriate rate constants to fit the slow diffusion controlled process.

The third approach is that defined by van Krevelen and co-workers (8, 9). They postulate a mathematical scheme to define not only the pyrolytic weight loss curves, but other coal pyrolytic phenomenon. This approach assumes that the decomposition of a bituminous coal can be distinguished into three successive reactions; formation of an unstable intermediate phase (metaplast) which is (partly) responsible for the plastification and transformation of this intermediate into semi-coke and finally into coke with three individual rate constants.

In addition to the assumption of one unimolecular decomposition the following assumptions are made in the three models. Case I, Berkowitz; (1) an undefinable equation of state of the product gases in the pore structures, (2) a diffusionally controlled rate loss which can not be treated rigorously, and (3) an assumed time of completion of pyrolysis which determines the activation energy. Case II, Pitt; (1) a value for the frequency factor "a", (2) the initial concentration of all volatile species is the same, (3) a large number of independent unimolecular decompositions of different activation energies. Case III, van Krevelen; (1) an initial depolymerization to unstable intermediate (metaplast) which decomposes to give gas, (2) equality of rate constants for formation and decomposition of metaplast and (3) the occurrence of a second (semi-coke) decomposition which produces additional gas.

Berkowitz found that significant differences existed between the weight loss-time curves for a -10 to +28 mesh coal and a -60 mesh coal. In our laboratory representative samples of -40 to +60 and -200 to +250 mesh coals were pyrolyzed. The weight loss time curves were identical. It is possible that heat distribution and thermal conductivity may be important with larger particle sizes.

In Pitt's model (Case II) it is assumed that the independently decomposing coal molecules have a distribution of activation energies for decomposition between E and $E+dE$. The number of undecomposed molecules remaining after some time t is given by the equation:

$$n_t = n_0 \int_0^{\infty} f(E) e^{-At} e^{-E/RT} dE$$

Mathematically assuming an energy distribution from zero to infinity and plotting a range of activation energies, the data give a broad maximum in the distribution curve in the energy range 50 to 55 kcal/mole.

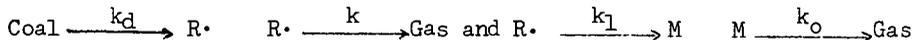
An alternate treatment using Pitt's model gives the equation:

$$x = \sum_{i=1}^j B_i - \sum_{i=1}^j B_i e^{-k_i t}$$

where j decompositions occur. Using Pitt's assumptions of equal initial concentration of volatile matter a curve analogous to Figure 4 can be constructed. From k_1 for our run 17/R (682°K), an activation energy of 51.6 kcal/mole is obtained. From k_2 the activation energy is 55.2 kcal/mole. For run 24/R (770°K), the respective values are 55.2 and 61.4 kcal/mole. The one disadvantage of Pitt's model is the assumption of equal initial concentration of all the volatile species. If the species pyrolyzed were large a more tenable assumption is equal k_i 's (equal activation energies). If so, the above equation reduces to simple first order kinetics and the initial concentration of B_1 is unimportant.

In van Krevelen's model (Case III), the assumption that the rate constants k_1 and k_2 are equal and that one half of the gas evolved is from each of two steps does not result in a good fit of the experimental curve, according to Pitt (6). The problem can be solved by modifying

slightly the van Krevelen model to permit an estimation of the gas produced in each step. Mathematically the final expression is the same as the integrated form for a consecutive reaction except that the fraction of gas produced is defined by a ratio of rate constants. The modified model consists of the following steps:



and $M \xrightarrow{k_2} \text{Coke}$, where $R \cdot$ is a reactive intermediate similar to van Krevelen's metaplast and M is equivalent to semi-coke; a steady state is assumed for $R \cdot$. By making certain simple approximations k_d can be determined from Figure 4. From the points of an Arrhenius plot, the variation in k_d with temperature gives the least square equation of $\log_e(k_d) = -11.1/T + 12.7$ which gives an activation energy of 22.1 kcal/mole and a frequency factor of 3.3×10^5 . If $k_o \cong k_2$, then $k_o + k_2$ corresponds roughly to k_3 of the van Krevelen model or k_f discussed previously. This means that the activation energy for the second step is very small (~ 2.4 kcal/mole). Pyrolysis could not account for the second step.

A new model which fits the experimental data involves the following two assumptions. The decomposition follows a simple first order rate law; the decomposition exhibits first order dependence upon the number of surface sites (S :) available at any time.

This model is based upon the earlier worker's observations and data cited and upon additional experimental data. In the pyrolyses conducted in this laboratory, the calculated residence time of volatile products is 9.3 seconds. Analyses of the nitrogen carrier gas stream utilizing an F and M model 720 Chromatograph and a Consolidated Electrodynamics Model 21-620 Mass Spectrometer showed no detectable low molecular weight hydrocarbons. The usual distillate was a tar mist. The product gases were frozen out in a liquid nitrogen cooled trap and analyzed. The total hydrocarbon and carbon dioxide concentration was determined to be 1.8% with CH_4 , C_2H_6 , C_3H_8 , $\text{C}_4\text{-C}_6$ and higher hydrocarbons being present in the ratio 80:60:62:129. The gas analysis indicates that in addition to the CO_2 and H_2O produced, the principle primary decomposition products were of high molecular weight. The light gases found may be due to secondary reactions. These analytical data strongly suggest that large molecules in the coal are fragmented to produce the primary products, probably in a single bond breaking, unimolecular reaction.

The second postulate involves a first order dependence upon surface sites; the pyrolysis reaction would be written $S: + (1-Z) \xrightarrow{k_o} Z + S:$. The differential equation defining the rate is: $dZ/dT = k_o (1-Z)(S:)$. The second postulate requires that $d(S:)/dZ = -b(S:)$ which on integration gives $(S:) = e^{-bZ}$. Substituting one obtains $dZ/dT = k_o(1-Z)e^{-bZ}$. From Eyring's rate theory (14) the rate constant $k_o' = \frac{kT}{e} \frac{-\Delta F^\ddagger}{RT}$ where k is Boltzmann's constant and h is Planck's constant. ^hIf the free energy of activation varies in a linear manner with the amount pyrolyzed, $\Delta F^\ddagger = \Delta F_o^\ddagger + qZ$. If q is a function of the entropy of activation only, i.e. of the relative complexity of the activated complex to the undecomposed

reactant, the temperature dependence of entropy cancels when this equation is substituted into Eyring's equation. If this is substituted into a unimolecular rate equation, the equation $dZ/dT = k_0 (1-Z)e^{-bZ}$ results where b is an entropy dependent term or $dZ/dT = (kT/h)e^{-\Delta F^\ddagger/RT}(1-Z)e^{-bZ}$. A plot of $\log \frac{dZ/dT}{T(1-Z)}$ versus Z should give a straight line of slope $b/2.3$.

If the model is correct the slope should not be temperature dependent. In Figure 9 the appropriate plots are represented from 0 to 75% completion. As can be seen, excellent point linearity and slope agreement at different temperatures, are found, especially for the lower temperature curves.

At the lower temperatures linearity is observed for 90% of the pyrolysis. At higher temperatures a departure from linearity occurs at 75% completion. This might indicate a break down of the coal surface at higher temperature (6) or an increase in secondary reactions.

From the intercepts of Figure 9, Figure 10 was constructed. The heat of activation was found to be 55.8 kcal/mole. The intercept is 13.51. This corresponds to a very small positive entropy of activation or to a frequency factor of about 10^{14} , a value to be expected from theoretical considerations. The activation energy is of the right magnitude for bond breaking reactions.

Van Krevelen's observation is most germane: "Any kinetic interpretation is much too simple to provide a complete description of the complicated decomposition process; therefore, it is more correct to regard it as a mathematical model which does not pretend to be more than an aid for obtaining a semi-quantitative description of the experimental results.

Appreciation is expressed to the Office of Coal Research which, with the State of Utah co-sponsors this research. We are grateful also for the advice and counsel given by Dr. R. I. Reed and Dr. Larry L. Anderson in the interpretation of the data.

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