

Decomposition Kinetics of a Phenolic-Carbon Composite. II. Rate Relationships

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Synopsis

The isothermal decomposition of a phenolic resin in a phenolic-carbon cloth composite was measured in air at 0.1 to 0.2 torr over the temperature range 104-718°C. Two decomposition rate relationships are presented that can be used to predict decomposition. One assumes two second-order consecutive rate-controlling reactions, and the other assumes a diffusion-limited second-order reaction. Two rate constants govern each relationship, one being operative during the initial decomposition stages, and the other during the final stages. Evidence is presented to support the applicability of both relationships to predict decomposition over the entire temperature range studied. Arrhenius plots of the rate constants consist of several segments linearly connected. Activation energies and frequency factors computed from these segments cover a broad range of values. The activation energies are used to correlate the temperature ranges with the predominant products formed in these ranges.

INTRODUCTION

Phenolic resins have been one of the earliest material sources for solid thermal insulators. Detailed studies concerned with their thermal decomposition, however, have appeared only in recent years.¹⁻¹⁰ Several of these studies¹⁻⁷ have shown clearly that a very large number of volatile decomposition products are formed. Some are thermally induced, e.g., water, which is formed in the postcuring process, and formaldehyde, which is a reverse-condensation product. Others are thermo-oxidatively induced products, such as carbon monoxide and carbon dioxide. The molecular structures of these products indicate that other nonvolatile decomposition products must also be formed as intermediates for those that volatilize.

Progress has also been evident in resolving the decomposition kinetics.⁶⁻¹⁰ The complexity of phenolic-resin decompositions which involve many competitive and consecutive reactions, as well as residual polymerization, makes it difficult, however, to obtain precise information concerning their kinetics. A strong interest in the kinetics exists, nevertheless, stemming in recent years from the application of phenolics to the fabrication of nose tips and heat shields for reentry vehicles. The lack of information on the decomposition kinetics has led, therefore, to the development of rate relationships based on general principles in kinetics. These relationships have, in large

measure, assumed first-order kinetics, with little if any attention to the decomposition mechanism.

The complexity of the decomposition would suggest that rate relationships cannot be defined in a more realistic, yet tractable, form. However, special conditions are possible that permit more definitive rate expressions than the generalized forms in use which are not overly complex and which permit evaluation of the necessary parameters. The conditions and relevant assumptions are described below.

In processes that involve a series of reactions which may also be diffusion dependent if the medium is a solid or is nonhomogeneous, a spectrum of rates exists for the many steps in the series. One or a few of these rates may be sufficiently slow that the rate for the overall process will be controlled by the slowest steps. Decomposition rate measurements will then correspond to the kinetics of the rate-controlling reactions.

An added measure of simplification is possible if the concentrations of the chemical species in the rate-controlling steps are proportional to the resin weight. If the above assumptions pertaining to a limited number of rate-controlling reactions are applicable, then the requirements for determining reactant concentrations and rates are reduced to obtaining products of weight and a proportionality factor and time measurements.

The decomposition kinetics of a phenolic-carbon cloth composite was studied with these assumptions in mind. In a previous publication,¹¹ it was shown that the final stages of the decomposition could be characterized with second-order kinetics and an equilibrium expression for the amount of resin available for volatilization. Heats of reaction obtained from the equilibrium data were correlated with hydrogen bonding in the products and the oxidative degradation of the resin.

The present report continues with this development. It is concerned with the derivation of rate relationships that predict decomposition rates which correlate well with experimental data. It is understood that, at best, these relationships only approximate a very complex system and that they are, more likely, only empirical relationships that conform with observations.

Two rate relationships were found that provide this correlation. Both assume second-order kinetics for the final stages of the reaction, a condition supported by observed data. One expression assumes a diffusion-limited second-order reaction and the other assumes two rate-controlling consecutive second-order reactions. Other possible mechanisms were also explored; none provided the same level of correlation as those described in this report.

Activation energies and frequency factors were computed from rate constants obtained during the initial and final stages of the decomposition. These vary with time and temperature and cover a very broad range of values. Correlations of these energies with possible products are made.

The phenolic-carbon composite whose decomposition was studied was prepared from a resin of the CTL-91LD or SC-1008 type and a high-purity

carbon cloth, such as Hitco SS1641. Isothermal decompositions were measured over the temperature range of 104°–718°C at air pressures of 0.1 to 0.2 torr. Additional material and experimental information are available in the preceding publication.¹¹

KINETICS

Reaction Order

Initial studies of the decomposition showed that the final stages of the decomposition followed second-order kinetics. The kinetics for the initial stages, however, were less definitive, although low-temperature studies indicated that the reaction order was approximately one. Figure 2 in the previous publication¹¹ shows representative second-order rate constants which vary with time and shows that constant values are realized during the final stages of the decomposition.

Since the objective for this study was the derivation of rate relationships that could predict decomposition, it was desirable to modify the second-order kinetics with additional terms so that rates could be predicted over the entire decomposition time period. Two rate relationships evolved from this study which fulfill this requirement. They are described in the following sections.

Diffusion-Limited Second-Order Kinetics

A rate relationship which provides good correlation between computed and observed decomposition rates was obtained by assuming the decomposition to be a diffusion-controlled reaction. This assumption appeared reasonable, since diffusion would be restricted by the carbon fibers and the crosslinked three-dimensional network that is present in phenolic resins. The second-order nature of the rate-controlling decomposition reaction suggested that two reactive groups were involved in the decomposition reaction. Since bimolecular reactions would depend on the mobility of the reacting groups, diffusion could very well influence the reaction rate.

The kinetics of diffusion-controlled bimolecular reactions have been studied by Waite.¹² He derived several rate relationships for these reactions, one of which has been modified for use in this study:

$$-\frac{d\left[\frac{w_\infty - w}{w_\infty}\right]}{dt} = k \left[1 + \frac{r_0}{(\pi Dt)^{1/2}} \right] \left[\frac{w_\infty - w}{w_\infty} \right]^2 \quad (1)$$

where w_∞ = maximum weight fraction of the composite lost at a particular temperature; w = weight fraction of the composite lost at time t ; k = rate constant; r_0 = radius of a sphere within which reaction will occur if reactants are present; and D = diffusion coefficient.

Integration of eq. (1) gives

$$\frac{1}{w_\infty - w} - \frac{1}{w_\infty} = \frac{kt}{w_\infty} \left[1 + \frac{S}{t^{1/2}} \right] \quad (2)$$

where

$$S = \frac{2r_0}{(\pi D)^{1/2}}$$

Equation (2) differs from the conventional second-order relationship

$$\frac{1}{w_\infty - w} - \frac{1}{w_\infty} = \frac{k't}{w_\infty} \quad (3)$$

where k' = rate constant in which

$$k' = k \left[1 + \frac{S}{t^{1/2}} \right] \quad (4)$$

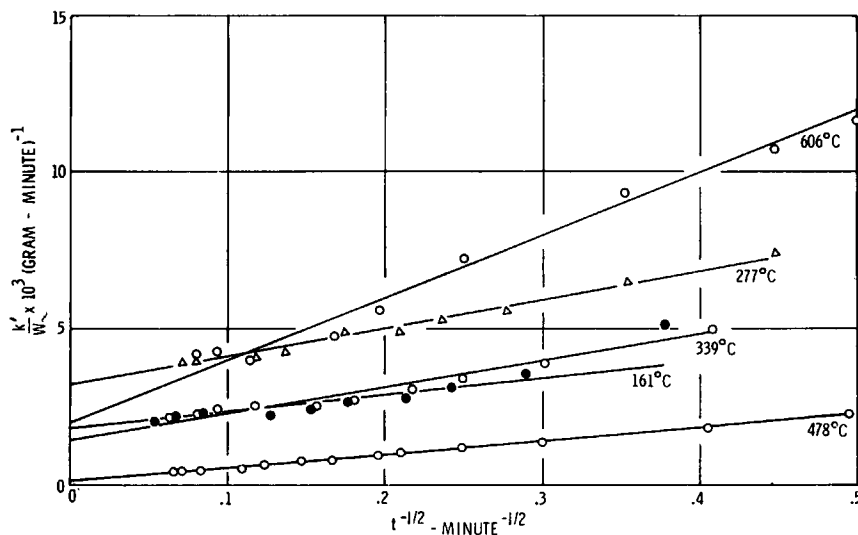


Fig. 1. Correlation of experimental data with eqs. (2) and (4) in terms of linear relationship predicted by these equations. For 161°C, ordinate multiplier is 10^4 .

A characteristic property of the diffusion-limited rate expression is the dependency of the rate constant on time. In the early stages of the decomposition, when t is small, values for k' will be larger than those in the final stages. Also, the value for S will determine the extent to which time will affect k' .

Plots in Figure 1 show the relevancy of eqs. (1), (2), and (4) to phenolic-resin decomposition and permit evaluation of the constants. Figure 1 utilizes eq. (4), which is in the form of a linear relationship with respect to $t^{-1/2}$, and provides plots of k'/w_∞ versus $t^{-1/2}$ over a broad temperature range. Values for kS and k were obtained from the slopes and intercepts of the plots, respectively.

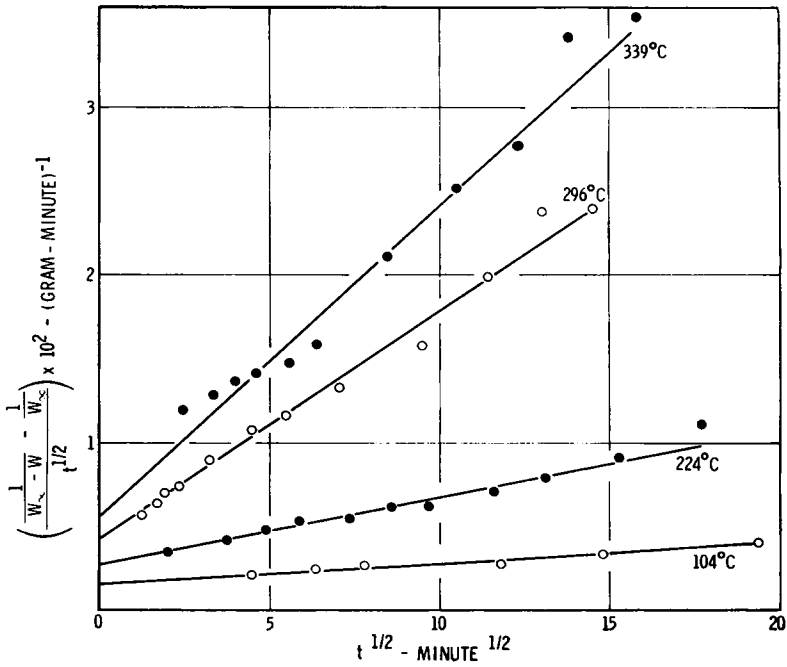


Fig. 2. Correlation of experimental data with eqs. (2) and (5) in terms of linear relationship predicted by the equations.

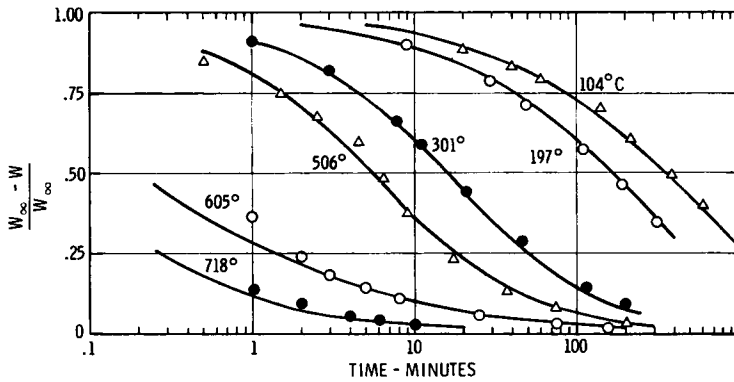


Fig. 3. Comparison of computed and experimental decomposition data. Computed values were obtained from eq. (2).

Equation (4) is more useful during the initial stages when values for t are small and those for $t^{-1/2}$ are large. For large values of t , kS and k were evaluated from the following expression:

$$\left[\frac{1}{w_\infty - w} - \frac{1}{w_\infty} \right] / t^{1/2} = \frac{k}{w_\infty} [t^{1/2} + S] \tag{5}$$

which is derived from eq. (2). It is also in the form of a linear relationship in which the left-hand term varies linearly with $t^{1/2}$. It was used for the lower temperature studies where decomposition times were longer. Representative plots are shown in Figure 2.

The ability of eq. (2) to predict weight loss is shown in Figure 3, which is a comparative plot of computed values for $(w_\infty - w)/w_\infty$ (solid line) and experimental data (circles). Values for kS and k were determined from plots similar to those in Figures 1 and 2.

Kinetics for Consecutive Bimolecular Reactions

An alternate rate relationship for the decomposition can be derived from the assumption that the decomposition consists of two consecutive rate-controlling bimolecular reactions. Consecutive rather than parallel reactions are assumed because intermediate products are known to exist.¹⁻⁷ In addition, the presence of the equilibrium in the reaction sequence leading to volatile products¹¹ also suggests consecutive rather than parallel reactions.

The reactions may be expressed as follows:



where A is a reactive group in the resin which is transformed to B; B is an intermediate which is converted to C; C is lost through nonrate-controlling reactions by volatilization; and k_a and k_b are the respective rate constants.

The rate equations which describe reactions (6) and (7) are developed below, integrated, and put in a form that permits the computation of values for resin weight loss. Validity for the kinetic expressions is established by comparing computed with experimental values.

The rate equations that are assumed to govern the decompositions are

$$-\frac{d[A]}{dt} = k_a[A]^2 \quad (8)$$

$$\frac{d[B]}{dt} = \frac{k_a}{2}[A]^2 - k_b[B]^2 \quad (9)$$

$$\frac{d[C]}{dt} = \frac{k_b}{2}[B]^2. \quad (10)$$

The integration of eqs. (8) through (10) to obtain an expression in terms of [C] has been reported by Chien.¹³ An alternate integrated form is given here, since it is the expression used in the computer program for this study. The expressions are interconvertible.

Integration of eq. (8) provides an expression for [A] as a function of time and the initial concentration, $[A]_0$:

$$[A] = \frac{[A]_0}{1 + k_a[A]_0 t} \quad (11)$$

Substituting this expression into eq. (9) and integrating provides the following expression for [B],

$$[B] = \frac{[A]_0}{2\gamma} \left(\frac{1 - \gamma^{-\alpha}}{\lambda_1 \gamma^{-\alpha} - \lambda_2} \right) \quad (12)$$

where

$$\begin{aligned} \alpha &= (1 + 2k_b/k_a)^{1/2}, \\ \gamma &= (1 + k_a[A]_0 t), \\ \lambda_1 &= \frac{1 + (1 + 2k_b/k_a)^{1/2}}{2} \text{ and } \lambda_2 = \frac{1 - (1 + 2k_b/k_a)^{1/2}}{2}. \end{aligned}$$

Since the resin initially available for decomposition, A, is converted to B and C, it follows that

$$[A]_0 = A + 2B + 4C \quad (13)$$

or

$$[C] = \frac{1}{4}([A]_0 - [A] - 2[B]). \quad (14)$$

Substituting the expressions for [A] and [B] in eqs. (11) and (12) into eq. (14) gives the following expression for [C]:

$$[C] = \frac{[A]_0}{4} \left\{ 1 - \gamma^{-1} - \gamma^{-1} \left(\frac{1 - \gamma^{-\alpha}}{\lambda_1 \gamma^{-\alpha} - \lambda_2} \right) \right\} \quad (15)$$

The concentration units for C will be determined by the units for A, since the terms within the bracket are dimensionless. The concentration units for A and C can be expressed as the moles or the grams of reactive groups per gram of composite which decompose and which are subsequently lost by volatilization. If expressed as grams/gram of composite, then $[A]_0$ is equivalent to w_∞ in eqs. (2) and (3). For extended time periods when A is depleted, the decomposition rate will be determined by eq. (10), which on integration gives an equation equivalent to eq. (3) with $[B] = (w_\infty - w)$ and $[C] = w$. Under these conditions, $k_b = k' = k$.

Values for w_∞ and k' were obtained from a rearranged form of eq. (3):

$$\frac{t}{w} = \frac{t}{w_\infty} + \frac{1}{w_\infty k'} \quad (16)$$

Equation (16) is a linear relationship between t/w and t with a slope of $1/w_\infty$ and an intercept of $1/k'w_\infty$. Linear plots obtained from this equation gave values for w_∞ which compared well with experimental data.¹¹ The intercepts, however, did not give values for k' that were as precise as desired. More precise values were obtained by averaging the limiting values of k' at extended times where constancy was apparent.¹¹

Values for $[A]_0$, k_a , and k_b are required for the evaluation of [C] in eq. (15). Of these three terms, only those for k_a are not available. No direct

or independent method for evaluating k_a was obvious. Assumed values were therefore used in eq. (15), and computed weight loss values were plotted and compared with experimental data for a best fit.

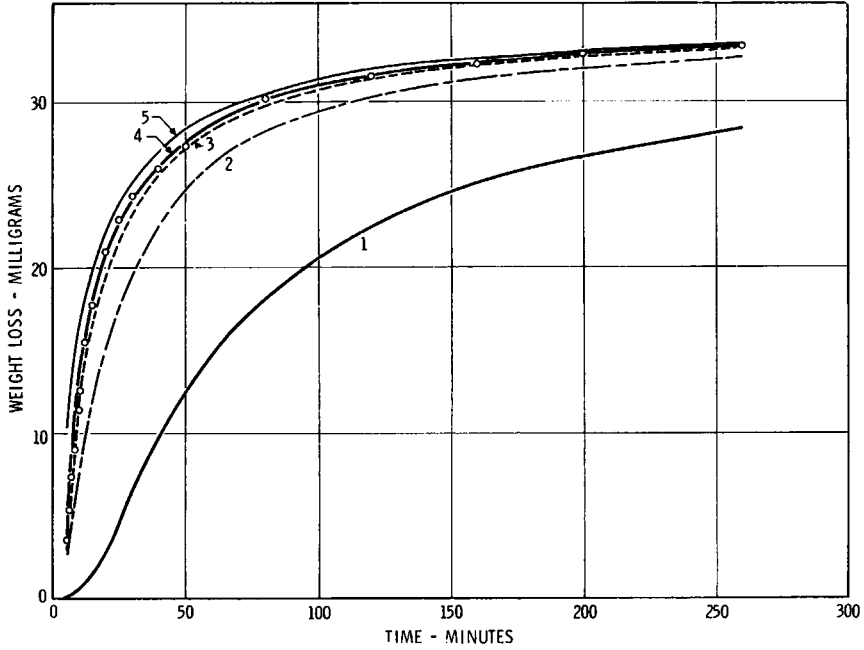


Fig. 4. Estimation of a value for k_a for eq. (15) by substituting assumed values in this equation and comparing with experimental values. Decomposition conducted at 338°C: (1) $k_a = 0.001$; (2) $k_a = 0.01$; (3) $k_a = 0.04$; (4) $k_a = 0.07$; (5) $k_a = \infty$.

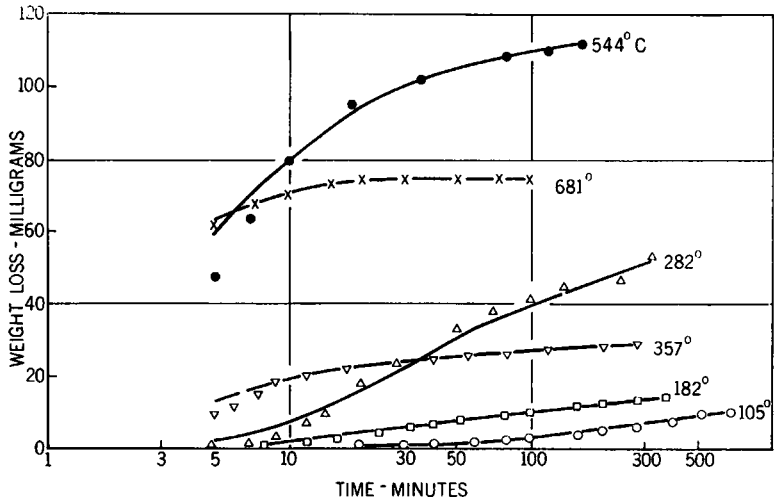


Fig. 5. Comparison of computed and experimental decomposition data. Computed values were obtained from eq. (15).

Figure 4 is a plot of this type for a decomposition studied at 338°C. It shows the effect of k_a values on computed weight loss values and is representative of plots obtained over the entire temperature range studied. Curves 1 through 4 were obtained with k_a values of 0.001, 0.01, 0.04, and 0.07 min⁻¹. Curve 4, which includes experimental data (open circles), provides the best correlation of experimental and calculated values. Curve 5 was obtained with a k_a value of infinity, or the condition under which the decomposition would be governed by a single second-order reaction. Figure 4 emphasizes the insensitivity of k_a and the difficulty of ascertaining precise values for k_a . It also shows that a slight displacement of the time scale would cause the experimental values to fall on curve 5. This displacement would be valid if the time required for temperature equilibration of the decomposing specimen were greater than calculated by the method shown in the previous publication.¹¹ It is believed, however, that the displacement more correctly represents a modified second-order reaction.

Additional evidence for the adequacy of eq. (15) to predict decomposition is given in Figure 5, where computed and experimental values correlate well over a broad temperature and weight loss range.

Effect of Temperature on Rate Constants

It was desirable to determine the effect of temperature on the rate constants. Two constants are involved in each of the two mechanisms that have been suggested; one is rate controlling in the initial stages of the decomposition, and the other, in the final stages. Although both mechanisms

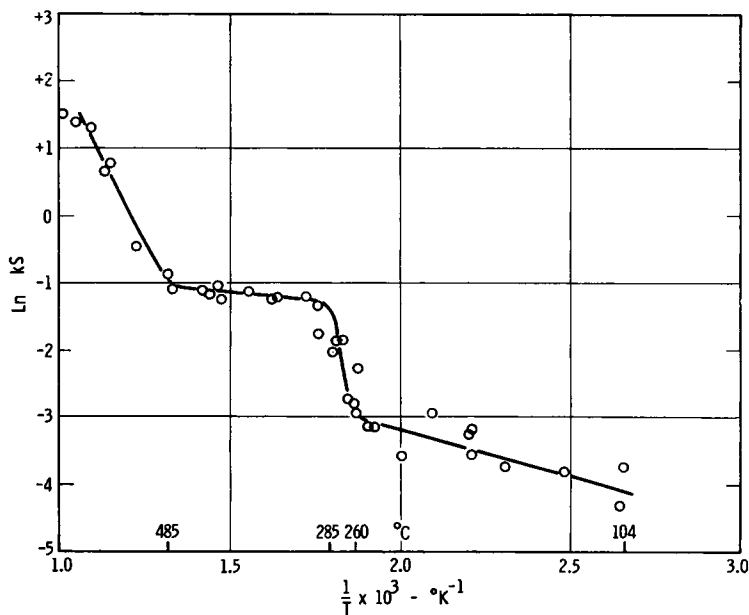


Fig. 6. Effect of temperature on decomposition rate constant kS .

share a common rate constant for the latter stages, i.e., $k = k_b$, the initial-stage constants, i.e., kS and k_a , differ. Since kS provided more precise values, it was examined for temperature effects.

Arrhenius plots of kS are shown in Figure 6. The values for kS rather than k and S , individually, are considered, since kS determines the initial decomposition rates, and it is these rates, and the effect of temperature upon them, that are of primary interest. The nonlinear variation of kS with temperature is significant, since it shows that four distinct temperature

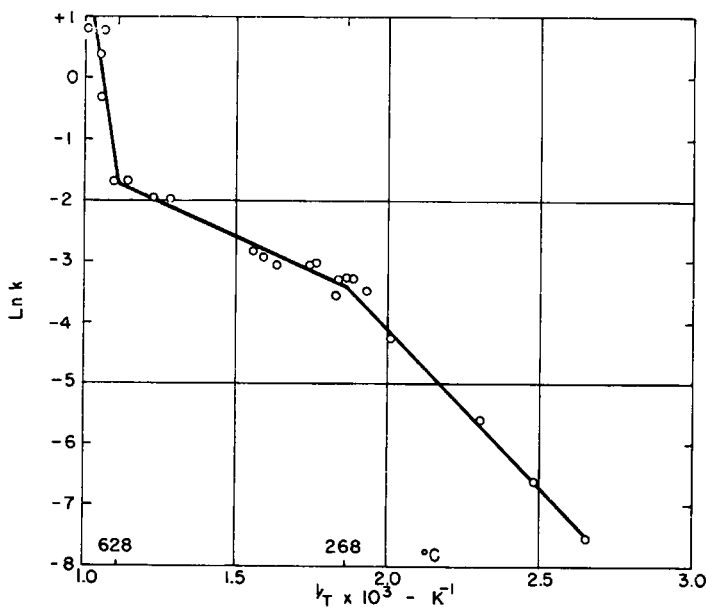


Fig. 7. Effect of temperature on decomposition rate constant k .

ranges exist: 104° to 260° , 260° to 285° , 285° to 485° , and above 485°C , each of which appears to be linear. The possibility that the sharp change between 260° and 285°C was due to a transition in the composite structure suggested an analysis with a differential scanning calorimeter. However, no thermally induced transition, other than decomposition, was evident up to 500°C , the temperature limitation of the instrument.

The rate constant for the final stage of the decomposition, k , also provides a nonlinear Arrhenius plot (Fig. 7) over the same temperature range. Because the values obtained for k are more scattered than those for kS , only those values are plotted in Figure 7 whose deviations from the mean are no greater than three times the mean deviation.

Figure 7 can also be divided into temperature ranges with linear segments: 104° to 268° , 268° to 628° , and above 628°C . Notable differences in the effect of temperature on kS and k are (1) the three discontinuities for kS in Figure 6 and two discontinuities for k in Figure 7 and (2) the temper-

ature at which each rate constant assumes its highest activation energy, i.e., 485°C for kS and 628°C for k .

Values for S were obtained from kS and k . Their relationship to the fundamental properties of r_0 and D ($S = 2r_0/(\pi D)^{1/2}$) was not investigated, since values for r_0 and D were not available. It is evident from Figures 6 and 7 that the variation of S with temperature is opposite to that for kS and k , since the slopes for kS are smaller than those for k . This behavior is consistent with the above relationship for S , since an increase in temperature will increase the diffusion coefficient D and therefore decrease S . The value for r_0 , the sphere radius within which reaction will take place, is assumed to remain reasonably constant.

Table I is a summary of the activation energies and frequency factors for the two rate constants. The activation energies provide a basis for correlat-

TABLE I
Activation Energies and Frequency Factors

| Temp. range, °C | Rate constant | Activation energy, kcal/mole | Frequency factor, min ⁻¹ |
|-----------------|---------------|------------------------------|-------------------------------------|
| 104-260 | kS | 2.6 | 0.58 |
| 104-268 | k | 10.2 | 4.8×10^2 |
| 285-485 | kS | 0.53 | 0.48 |
| 268-628 | k | 5.0 | 3.4 |
| 485-718 | kS | 21.0 | 3.0×10^5 |
| 628-718 | k | 50.0 | 1.8×10^{11} |

ing the results from this study with those of the previous study¹¹ and those of Shulman and Lochte.⁶ Correlations were found between the activation energies, the temperature ranges in which they are applicable, the heats of reaction, and the threshold temperatures at which volatile decomposition products first appear.

The results reported by Shulman and Lochte⁶ show gross variations in the product activation energies for the two resins studied. The heating rates also influenced the product yields and the threshold temperatures at which products appeared. Nevertheless, their results are helpful in suggesting products that can be associated with the activation energies obtained in this study.

Shulman and Lochte report decomposition product distributions as a function of temperature. Their resin B corresponds more closely to the resin in this study than their resin D. Both resins, however, show that formaldehyde and water are the major products in the lower temperature range. They found that formaldehyde formation has an activation energy of 11 kcal/mole. This value is comparable to the 10.2 kcal/mole value obtained in the present study for k in the lowest temperature range (104°-268°C), suggesting that the decomposition product in this range is formaldehyde.

It is of related interest that the activation energy for kS over the same temperature range is 2.6 kcal/mole, and that the heat of reaction for the equilibrium associated with resin available for decomposition has, within experimental error, the same value, 2.2 kcal/mole.¹¹ The heat of reaction can be equated to the activation energy when the difference in the mean heat capacity of the reactants and products is zero,¹⁴ a condition which appears to be fulfilled in the present study.¹¹ The above correlations suggest, therefore, that the forward equilibrium reaction is associated with the initial release of formaldehyde by a low-energy process and the subsequent release by a higher-energy process.

An additional correlation between this study and that by Shulman and Lochte can be made from their observation that water is released at temperatures above 250°C. This observation suggests that the discontinuities at 260° and 285°C in Figure 6 are threshold temperatures for water evolution and that it is the major product in the 285° to 485°C temperature range. The activation energy for this range (Table I) in the initial stage is 0.53 kcal/mole, a value which is close to the heat of vaporization of water, 0.58 kcal/mole. The activation energy in the final stage of this temperature range increases to 5.0 kcal/mole, a value which does not correlate with values given by Shulman and Lochte.

A third product correlation can be drawn between this study (Fig. 7) and that of Shulman and Lochte. Figure 7 shows a discontinuity at 628°C and an activation energy of 50.0 kcal/mole above this temperature (628°–718°C). This energy can be correlated with a value of 45 kcal/mole obtained by Shulman and Lochte for carbon monoxide formation over the range 600°–700°C. Additional evidence for this correlation is suggested by the threshold temperature of about 350°C for carbon monoxide given by Shulman and Lochte. The experiment associated with this value is considered relevant, since carbon monoxide is the major constituent of the volatile products in the temperature range under consideration. The 350°C threshold temperature correlates with the 352°C discontinuity in the $\ln K$ versus $1/T$ plot in Figure 6 of the previous publication,¹¹ where K is the equilibrium constant for resin available for volatilization. The heat of reaction obtained from this figure, 15.3 kcal/mole, was related to the activation energy for the oxidation of methylene groups reported by Conley and co-workers.¹⁻⁴ Since carbon monoxide is an oxidation product and its weight loss appears to be related to methylene group oxidation, the precursor for carbon monoxide formation can be ascribed to oxidized methylene groups as suggested by these workers.¹⁻⁴

These results correlate with additional results obtained by Conley and co-workers. Their spectrophotometric studies of heated phenolic resin films have shown that water and formaldehyde are lower-temperature thermally induced products evolved from postcuring and reverse-condensation processes, respectively. Carbon monoxide, however, is a higher-temperature thermo-oxidative product that appears above 500°C.

Summary

Two rate expressions are presented for the decomposition of phenolic resins over the temperature range 104°–718°C. One assumes a diffusion-limited, second-order rate-controlling reaction; and the other assumes two second-order rate-controlling consecutive reactions. The decomposition predicted by both expressions correlates well with experimental data. Arrhenius plots of the rate constants show linear relationships over temperature range segments which are bounded by discontinuities in slope. Activation energies obtained from these plots are used to associate temperature ranges with the formation of specific decomposition products.

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