

Decomposition Kinetics of a Phenolic-Carbon Composite. I. Resin Available for Volatilization

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Synopsis

The isothermal decomposition of a phenolic resin in a phenolic-carbon cloth composite was measured at approximately 0.1 to 0.2 torr over the temperature range of 105°-718°C. The kinetics are initially first order and, in the later stages, second order. An analytic technique is provided for calculating the maximum quantity of resin which will volatilize during decomposition, thereby obviating the necessity of measurements for extended time periods. The amount of resin available for volatilization during decomposition varies with temperature and is in equilibrium with resin, which does not volatilize. Plots of the equilibrium constant versus the reciprocal absolute temperature show that two equilibria are involved: one which predominates up to 352°C and the other above this temperature. The heats of reaction are 2.2 and 15.3 kcal/mole. The first value is associated with hydrogen bonding and the second with decomposition and oxidation activation energies.

INTRODUCTION

The decomposition of a phenolic resin is a complex process which releases over 40 different volatile products.¹⁻⁷ The molecular structure of these products indicates that other nonvolatile materials are formed initially and that these act as intermediates for the volatile products. Thus, the total number of decomposition products is much greater than 40 and suggests that a series of consecutive and competitive reactions is involved in the decomposition process. These reactions would involve additional residual polymerization (since phenolic resins are usually not completely cured), thermal decomposition, and oxidation.

The complexity of the decomposition process is projected on its kinetics. Thus, a precise statement concerning the rate of decomposition would entail the gathering of considerable information. It would include the characterization of all reactions, determination of the kinetics for each, measurement of rate constants, determination of activation energies, etc.

The task of obtaining a detailed understanding of the decomposition kinetics for a phenolic resin, therefore, may be more formidable than is warranted by the existing interest in phenolic-carbon composites for heat shields, ablators, etc., unless a commitment has been made for a particular phenolic resin and precise decomposition information is necessary. How-

ever, the need still exists for less exacting kinetic expressions that would predict the weight loss of resin over a wide range of conditions. Such expressions would be useful for evaluating high temperature performance. It is this need which has prompted a study of the decomposition of the phenolic-carbon composite.

It would seem that the reaction kinetics for a series of competitive and consecutive reactions, such as occur in the decomposition of a phenolic resin, could not be expressed in a simple and readily applicable form. However, a rationale based on the following arguments can be formulated for the existence of such kinetics. In a chemical process governed by a large number of reactions within a solid matrix, a spectrum of reaction and diffusion rates can be expected to exist. One or more of these rates will be sufficiently slower than the others so that it will control the rate for the whole process over a specified temperature range. The chemical species and the particular rate-controlling reactions may not be known or readily identified, but if one of the reactants is initially present in the resin, its concentration can be expressed as a fraction of the total resin weight. Thus, the analytical chemistry requirements for the quantitative determination of reactants are reduced to weight measurements and the kinetic-expression requirements are obtained from one or a few reactions.

Studies of phenolic resin decomposition kinetics have been made by Heron,⁸ Madorsky and Strauss,⁹ Friedman,¹⁰ Shulman and Lochte,⁶ and Conley.⁷ The present study which was performed under isothermal conditions over the range of 105°–718°C, characterizes the decomposition with (1) second-order kinetics and (2) an equilibrium expression for the amount of resin available for volatilization. Heats of reaction obtained from the equilibria data are correlated with hydrogen bonding in the products and the oxidative degradation of the resin.

This study was undertaken to provide kinetic expressions for predicting resin weight loss as a function of time and temperature. In a subsequent report, the decomposition data will be used to provide more sophisticated rate expressions which predict weight loss values showing very good correlation with experimental data over the above temperature range and which will provide a deeper insight into some aspects of the mechanism.

EXPERIMENTAL

Material

The phenolic-carbon composite was prepared from a phenolic resin of the CTL-91LD or SC-1008 type and a high-purity carbon cloth such as HITCO SS1641. The prepared laminate contained 34%–38% resin solids. Stage curing of the laminate was performed over the temperature range of 82°–135°C for 13 hr. Postcuring was performed for 4.5 days at 135°–191°C. The density of the cured laminate was 1.50 g/cc.

Apparatus and Methods

An Aminco Thermo-Grav instrument was used for the isothermal decomposition rate study. The furnace was preheated before inserting the sample tube, thereby reducing thermal equilibration time to 12 to 15 min. Temperature fluctuation following thermal equilibration was approximately $\pm 1.5^\circ\text{C}$.

The amount of resin which decomposed varied with temperature. The sample size was, therefore, varied from about 1.2 g at the lowest temperature to about 0.3 g at the highest temperature, thereby meeting sensitivity

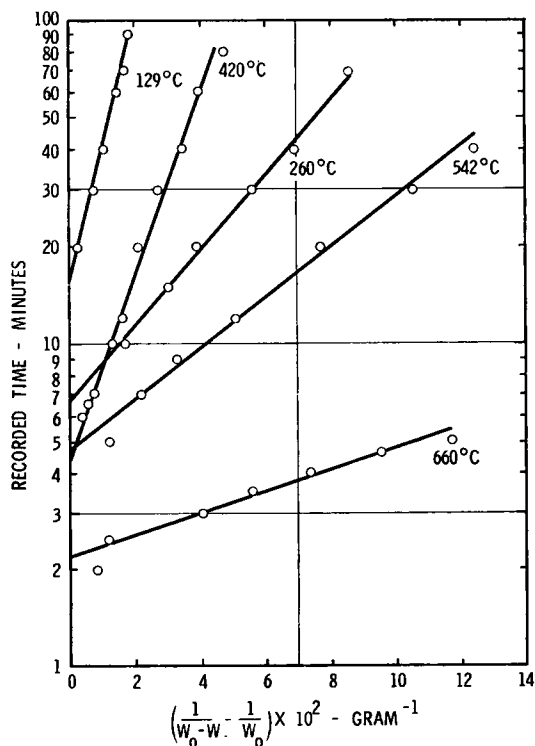


Fig. 1. Determination of corrected zero times from recorded times.

requirements and yet not exceeding the chart and other instrumental limitations.

Solid resin as cubes and platelets, rather than powder, was used to provide results which would approximate the proposed applications for the resin. The platelets were cut normal and perpendicular to the laminate direction. Some samples were stored under vacuum in the presence of a drying agent. The sample variations did not effect the decomposition rate, however.

Because the samples did not attain thermal equilibrium in a time period which was small compared to the initial time measurements, it was neces-

sary to assign corrected zero times for each decomposition. Plots of the following empirical expression

$$\log(\text{recorded time}) \text{ versus } 1/(w_\infty - w) - (1/w_\infty)$$

served this purpose: where w_∞ = maximum weight loss occurring at a particular temperature and w = weight loss at time t . An extrapolation of these plots to zero weight loss provided the time corrections to be applied to the recorded times for determination of the corrected decomposition times. Figure 1 shows several representative plots. In almost all cases it was found that this relationship was linear during the initial time periods of the decomposition. These periods extended well beyond the 12- to 15-min thermal equilibration period, except for the highest temperatures. Even at the higher temperatures, where the decomposition rate approached the point at which most of the weight loss occurred in times equivalent to the thermal equilibration period, linearity still existed.

The decompositions were carried out under continuously pumped vacuums of 0.1 to 0.2 torr to obtain decomposition in a minimum of oxygen. Pressures increased above this range, however, during the initial stages of the decomposition. At the highest temperatures, pressures of about 2 torr were realized. These decreased as the initially high decomposition rate decreased.

KINETICS

Reaction Order and Resin Available for Volatilization

Although others have suggested first-order⁶⁻⁹ and fifth-order¹⁰ decomposition kinetics, the isothermal decompositions performed in this study indicates that the initial stage of the decomposition is first order kinetically and the latter stage second order. This study also shows that the quantity of volatile matter generated during decomposition, i.e., weight loss, varies with temperature and can be expressed in terms of an equilibrium constant.

The relationship between temperature and the quantity of volatile matter generated was investigated in the following manner. It was impractical to perform the weight loss measurements for extended time periods to ascertain the limiting weight loss because of the long time periods required (days at the lowest temperatures). Instead, it was found more expedient to use the second-order kinetic relationship to calculate these values after it was established that the calculated and measured weight loss values were equivalent.

The second-order relationship can be expressed as

$$-\frac{d(w_\infty - w)/w_\infty}{dt} = k \left(\frac{w_\infty - w}{w_\infty} \right)^2 \quad (1)$$

where w_∞ = maximum weight loss occurring at a particular temperature, w = weight loss at time t , and k = rate constant. Integration of eq. (1) gives

$$\frac{1}{w_\infty - w} - \frac{1}{w_\infty} = \frac{kt}{w_\infty} = k't \tag{2}$$

where $k' = k/w_\infty$.

The correlation between eq. (2) and the data from the present study is shown in several plots in Figure 2 where k' is plotted against time. It is evident that eq. (2) is applicable during the latter portions of the decomposition and can, therefore, be used to determine the value of w_∞ . It was evaluated by rearranging eq. (2) into the following form:

$$\frac{t}{w} = \frac{t}{w_\infty} + \frac{1}{w_\infty k'} \tag{3}$$

Equation (3) shows that a plot of t/w versus t should be linear with a slope of $1/w_\infty$. The applicability of eq. (3) is demonstrated in Figure 3, where several plots covering a range of temperatures confirm the expected linear relationship.

To verify the above analytic method for evaluating w_∞ , the following alternate method was used. The desired quantity w_∞ was related to measured quantities w_t and w_r through the relationship

$$w_\infty = w_t + w_r \tag{4}$$

where w_t = measured weight loss at time t and w_r = residual weight loss normally not measured isothermally because of the required extended time periods.

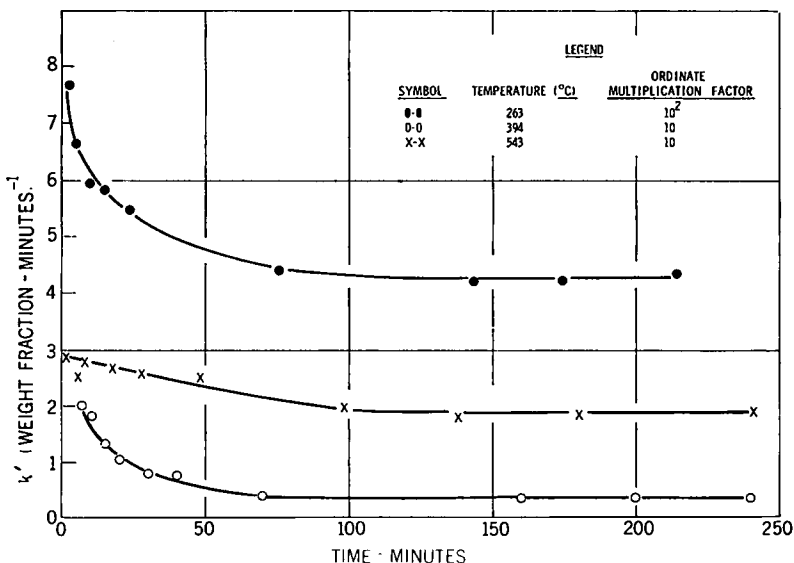


Fig. 2. Variation in k' values, obtained from eq. (2), with time.

It was found that values for w_r could be obtained from the thermographs of specimens which had previously been heated isothermally to obtain rate constant data. The method is shown in a representative thermograph, Figure 4. The discontinuity that occurs at approximately 405°C does not occur with specimens that have no prior isothermal heating histories. The weight loss at the discontinuity is interpreted as the residual weight loss

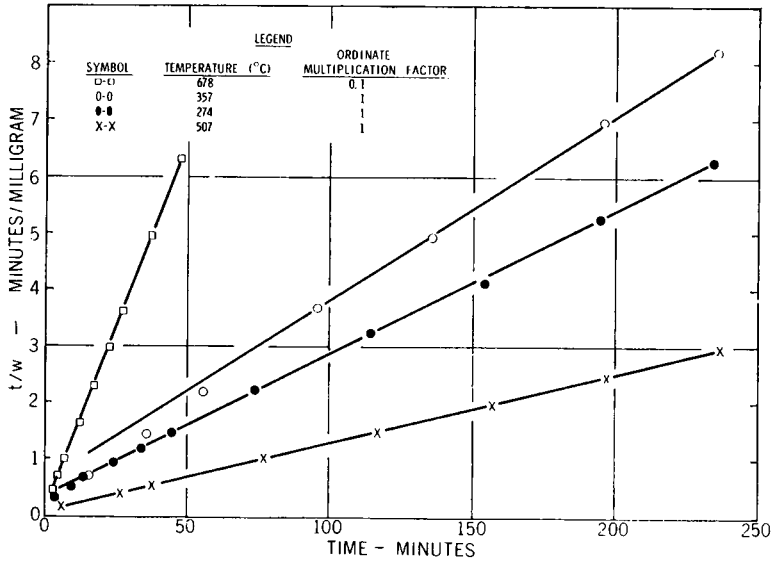


Fig. 3. Determination of resin weight available for volatilization (w_∞) from plots of t/w vs. t [eq. (3)].

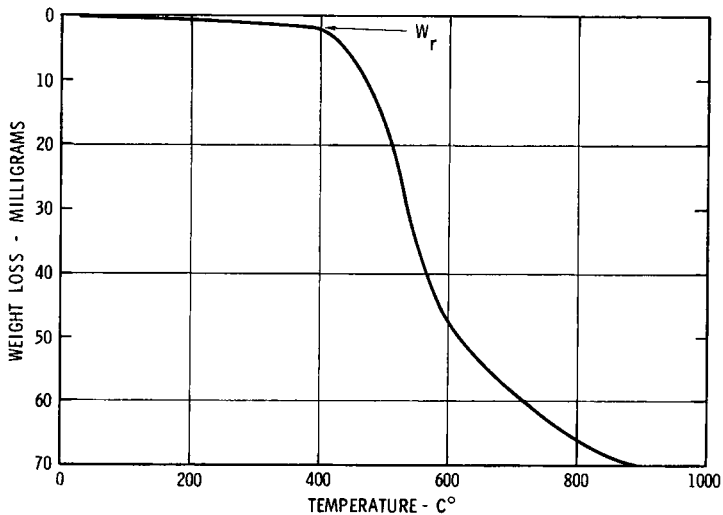


Fig. 4. Thermogravimetric analysis plot for a sample which has undergone isothermal decomposition. Heating rate 4°C/min.

TABLE I
Maximum Resin Available for Volatilization (w_{∞})

Isothermal decomposition temperature, °C	Values from eq. (3), mg	Experimental values, mg
130	12.1	12.8
181	17.7	18.3
305	24.1	24.6
359	34.4	31.5
394	53.7	50.6
434	74.3	72.4
479	87.6	80.9
544	67.6	62.7
612	41.1	40.4

w_r , for this temperature. The interpretation is verified with a comparison of values for w_{∞} obtained by this procedure with those computed from eq. (3), Table I. Although the correlation is not precise, no trends are evident and the mean deviation is only $\pm 3.4\%$.

Effect of Temperature on w_{∞}

The maximum resin weight that can be lost during decomposition, w_{∞} , is dependent upon the temperature at which decomposition takes place. The dependency is shown in Figure 5, where values for w_{∞} are expressed as the fraction of composite that can be lost. Figure 5 shows that only a fraction of the resin is available for volatilization during decomposition and that it varies with temperature. At the highest temperatures, this fraction is

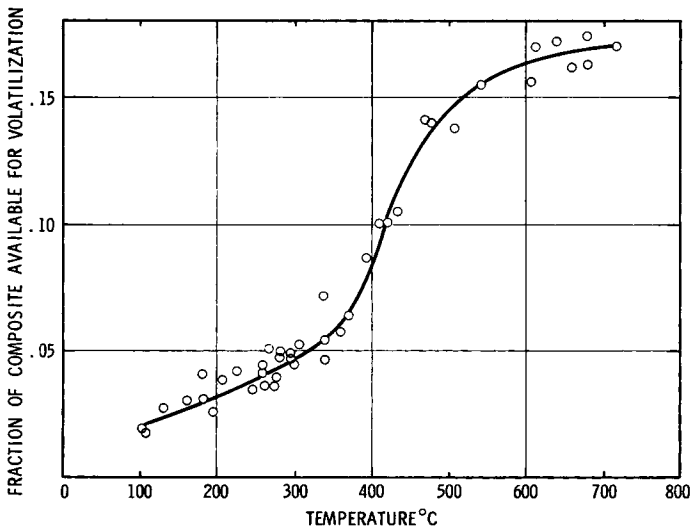


Fig. 5. Fraction of composite available for volatilization as a function of temperature.

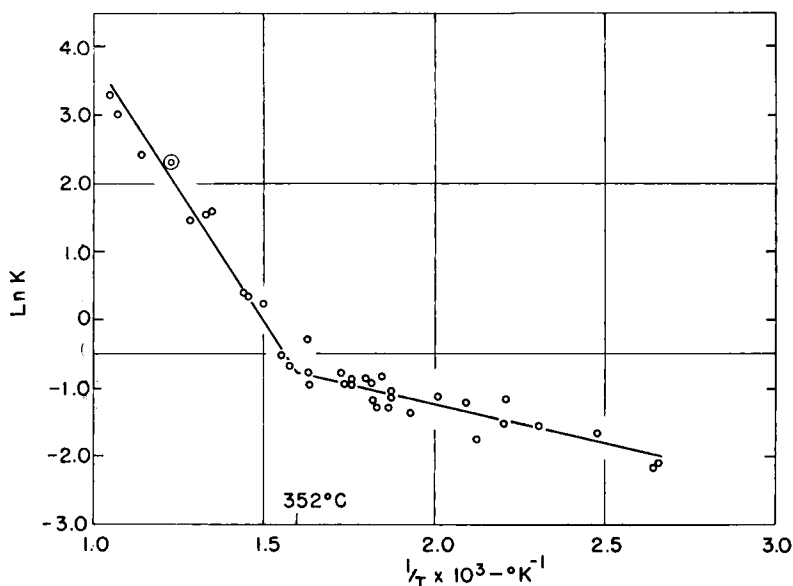


Fig. 6. Evidence for the equilibrium character of w_{∞} using eq. (6).

0.170 and is realized between 700°C and 800°C. The limiting character of this value was verified experimentally with the results from ten thermogravimetric analyses conducted up to 1100°C. The average weight fraction of material lost was 0.169 ± 0.004 . The material remaining consisted of char and carbon cloth.

The character of Figure 5 suggests that the fraction of resin available for volatilization at any particular temperature exists in equilibrium with the resin potentially available for decomposition at a higher temperature. Evidence favoring the existence of this type of equilibrium is found in the variation of an equilibrium constant K with changing temperature, defined as follows:

$$K = \frac{w_{\infty}}{w_{\infty \max} - w_{\infty}} \quad (5)$$

where $w_{\infty \max}$ = the maximum composite weight that will volatilize up to 1100°C.

The equilibrium character of the constant in eq. (5) is shown with the aid of a thermodynamic relationship which relates equilibrium constants to temperature:

$$-\ln K = \Delta H/RT + I \quad (6)$$

where ΔH = heat of reaction or enthalpy change, R = gas constant, T = temperature in °K, and I = integration constant. A plot of $\ln K$ versus $1/T$ should be linear and its slope should provide the average enthalpy change over the measured temperature range. The plot in Figure 6, obtained with equilibria data from this study, shows two linear relationships

over the 614°C temperature range. The enthalpy changes for the temperature ranges of 104°–352°C and 352°–718°C are 2.2 and 15.3 kcal/mole, respectively.

The existence of two linear relationships is consistent with the observations of Heron⁸ and Jackson and Conley.² They found that the residual resin remaining at the high temperatures and postcured resins are more resistant to decomposition. The high temperature resistance to decomposition is supported by the higher enthalpy value for the 352°–718°C range.

Enthalpy changes can be helpful in characterizing the types of reactions involved in equilibrium processes, especially when prior knowledge of these reactions is not available. The 2.2 kcal/mole value for the 104°–352°C temperature range implies that the resin available for decomposition involves very weak bonding. The presence of hydroxyl, methylene, and methylol groups in phenolic resins suggests the possibility that the weak bonding may be hydrogen bonds existing under equilibrium conditions. This is supported by evidence from (1) infrared spectrographic studies^{11–13} which show that hydrogen bonds exist between the phenolic hydroxyl groups and methylene groups, both intramolecularly and intermolecularly and (2) the enthalpy values for hydrogen bonds.

Enthalpy data for hydrogen bonds in phenolic resin structures have apparently not been reported. However, related compounds such as phenols, substituted phenols, and alcohols possess enthalpy values of 2 to 6 kcal/mole.¹⁴ Of interest is the enthalpy value of 1.2 kcal/mole for *p*-benzylphenol,¹⁵ a compound which corresponds most closely to the structures present in phenolic resins. This value compares well with the enthalpy value of 2.2 kcal/mole obtained in the present study.

Additional evidence is found in the observations that hydroxyl, methylene, and methylol groups are known to disappear in the curing process.^{2,6} It is doubtful, however, that the equilibrium under consideration involves the breaking of primary bonds, because the enthalpy changes would be considerably higher. Instead, it is believed that the equilibrium reaction involves the release of water and formaldehyde, which are products of the curing process and which have been trapped in the resin.

The plot in Figure 6 also shows an enthalpy value of 15.3 kcal/mole for the variation of w_{∞} with temperature in the temperature range of 352°–718°C. This value can be correlated with (1) the 15 and 18 kcal/mole values reported by Heron⁸ and Madorsky and Strauss,⁹ respectively, for the phenolic resin decomposition activation energy; (2) with the 16.7 and 15.6 kcal/mole values reported by Jackson and Conley^{2,3} for the oxidation of postcured phenolic resins; and (3) with the 14.5 and 16.8 kcal/mole values reported by Conley¹⁶ for the oxidation of polybenzyl, a compound structurally related to phenolic resins.

The relationship between activation energy and enthalpy (heat of reaction) is discussed by Benson.¹⁷ He shows that the heat of reaction can be equated to the activation energy when the difference in the mean heat capacities of the reactants and products is zero. The linearity of the plot in Figure 6 in the present study indicates that this difference is, at least,

close to zero, thus a correlation can be made.¹⁷ The correlation is of interest since it indicates that the resin available for volatilization is related to the oxidation of the resin. Hence, the oxidized material is in large measure the precursor for the volatile material in the resins of the present study. The results also indicate that thermal degradation, independent of oxidation, must be minimal over the entire temperature range studied. The variation in w_{∞} with temperature can therefore be related to the extent to which oxidative degradation takes place at various temperatures.

CONCLUSIONS

The decomposition rates of a phenolic-carbon composite which have been measured isothermally over the temperature range of 105°–718°C can be described during the later portion of the decomposition with second-order kinetics. The amount of resin available for loss by volatilization was computed from kinetic expressions and verified experimentally. This quantity was found to vary with temperature and to exist in equilibrium with resin which is not available for volatilization. The variation of the equilibrium constants with temperature shows that two equilibria exist and possess enthalpies of 2.2 and 15.3 kcal/mole. The first value suggests that one equilibrium may involve hydrogen bonding. The second value is associated with the oxidation degradation reactions.

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References

1. R. T. Conley and J. F. Bieron, *J. Appl. Polym. Sci.*, **7**, 103, 171 (1963).
2. W. M. Jackson and R. T. Conley, *J. Appl. Polym. Sci.*, **8**, 2163 (1964).
3. R. T. Conley, *J. Appl. Polym. Sci.*, **9**, 1117 (1965).
4. H. W. Lochte, E. L. Strauss, and R. T. Conley, *J. Appl. Polym. Sci.*, **9**, 2799 (1965).
5. H. L. Friedman, *J. Appl. Polym. Sci.*, **9**, 1005 (1965).
6. G. P. Shulman and H. W. Lochte, *J. Appl. Polym. Sci.*, **10**, 619 (1966).
7. R. T. Conley, *J. Macromol. Sci. (Chem.)*, **A1**, 81 (1967).
8. G. F. Heron, *Society of Chemical Industry (London), Monograph 13*, MacMillan, New York, 1961, p. 474.
9. S. L. Madorsky and S. Strauss, *Modern Plastics*, **38**, No. 6, 134 (1961).
10. H. L. Friedman, *J. Appl. Polym. Sci. C*, 183 (1963).
11. N. D. Coggeshall, *J. Amer. Chem. Soc.*, **72**, 2836 (1950).
12. T. Cairns and G. Eglinton, *Nature*, **196**, 535 (1962).
13. V. P. Pshenitsyna, A. N. Shabadash, and T. V. Fremel, *Dokl. Akad. Nauk SSSR, Phys. Chem. Section* (Engl. translation), **153**, 1027 (1963).
14. G. C. Pimental and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco, 1960.
15. A. Aikara, *Bull. Chem. Soc. Japan*, **33**, 194 (1960).
16. R. T. Conley, *J. Appl. Polym. Sci.*, **9**, 1107 (1965).
17. S. W. Benson, *Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960, p. 71.

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