

Quantitative Studies by Differential Scanning Calorimetry of the Reaction between Hydrogen Peroxide and Lignocellulose

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Synopsis

Heat of reaction and kinetic parameters were determined by differential scanning calorimetry for decomposition of hydrogen peroxide, reaction of hydrogen peroxide with lignocellulosic materials, glucose and pinitol, and for the reaction of the same materials with produced or introduced oxygen. The heat of decomposition of hydrogen peroxide obtained in N₂ (720 cal/g H₂O₂) was in fair agreement with literature data, considering the different temperature and pressure conditions. The heats of reaction of hydrogen peroxide and lignocelluloses were higher when determined in N₂ (1670–2500 cal/g H₂O₂) than in O₂ (1450–2020 cal/g H₂O₂) atmosphere. The activation energy for decomposition of hydrogen peroxide amounted to 20.3 kcal/mol in N₂ and 15.9 kcal/mol in O₂ with frequency factors of 5.7×10^9 and $3.7 \times 10^7 \text{ min}^{-1}$, respectively. The activation energies for the reaction of hydrogen peroxide and lignocellulosic materials tested were similar and not influenced by the atmospheric composition, ranging overall between 19.7 and 22.4 kcal/mol. The corresponding frequency factors ranged between 2.77×10^9 and 2.23×10^{11} .

INTRODUCTION

The validity of applying the mathematical expressions which describe the isothermal state of homogeneous processes to the dynamic state of heterogeneous processes is much in debate. Nevertheless, an increasing trend toward the use of thermal analysis, a dynamic method, for quantitative thermodynamic and kinetic studies, is apparent. This is due, in part, to the recent commercial introduction of highly sensitive and reliable thermal analytical instruments, and, in part, to certain advantages of these techniques (e.g., rapidity, simplicity, versatility, objectivity) over classical isothermal methods. As pointed out by Ozawa,¹ dynamic methods have another advantage over isothermal methods in that, for a system in which multiple reactions proceed concurrently, the characteristics of the reactions may be revealed by their dynamic behavior, i.e., the rate of heating of samples.

We have developed an experimental technique whereby the decomposition of hydrogen peroxide and the reactions between lignocellulosic materials and hydrogen peroxide can be studied using differential scanning calorimetry.^{2,3} The influence of various parameters on the thermal characteristics of these reactions was extensively covered by our previous publications.²⁻⁴ This paper will deal with the determination of the heat of reaction and of kinetic parameters of these reactions.

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THEORETICAL BACKGROUND

Heat of Reaction

The determination of ΔH , the enthalpy of a reaction from DSC (differential scanning calorimetry) or DTA (differential thermal analysis) data, has been widely practiced based on the proportionality between peak area and the change in enthalpy expressed in the following equation:

$$\Delta H = KA/m \quad (1)$$

where ΔH is change in enthalpy, A = peak area, m = the mass of the sample, and K = the calibration factor.

In practice, the accuracy of ΔH and the proportionality between ΔH and A are influenced by several factors, including temperature range, geometrical configurations of the sample, pressure, and chamber atmospheric conditions. No mathematical expression could include all these factors. Therefore, the only method to insure reliable and consistent results is to calibrate the instrument against known standard materials for given experimental conditions, i.e., to determine K . For a DuPont DSC, K is related to several instrumental parameters:

$$K \text{ (mcal/cm}^2\text{)} = \frac{BW\Delta q}{6.452} \quad (2)$$

where B = time setting (s/cm), W = cell calibration coefficient (dimensionless), Δq = calorimetric sensitivity [Y -axis range, (mcal/s-cm)]. Using this expression, eq. (1) becomes

$$\Delta H = \frac{A}{m} \frac{BW\Delta q}{6.452} \quad (3)$$

Since B and Δq are the instrument settings, W is the dependent variable which must be calibrated for the experimental conditions of interest. As indicated in our previous paper, DSC of H_2O_2 -treated lignocellulosic materials under atmospheric conditions yielded two consecutive peaks, one exotherm and one endotherm. The order of appearance of these peaks depends on the pressure within the sample pan.² The exotherms are due to hydrogen peroxide decomposition or reaction between hydrogen peroxide and lignocellulose, while the endotherms are due to the evaporation of hydrogen peroxide or of water. Exotherms and endotherms overlap each other at ambient pressure. In order to satisfactorily study the reaction between hydrogen peroxide and lignocellulose, these two processes have to be separated. This was done by elevating the pressure, thereby shifting the endotherms to higher temperatures.³ Accordingly, the cell calibration coefficient W should be calibrated as a function of pressure against several standard materials which have melting points within the temperature range of interest.

Although a considerable number of reports exists on the phase transitions and chemical reactions studied by thermal analysis under elevated pressure,⁵⁻¹³ very few quantitative determinations of the enthalpy of transformations have been reported.^{8,12-15} Two factors probably account for this situation—the availability of only a few ΔH values experimentally determined under elevated pressure for

transformations useable as standards,^{16,17} and the experimental difficulties associated with thermal analysis under elevated pressure.^{14,15,18} Kamphausen^{12,13} has reported a calibration method and the heats of transformation for several organic compounds under elevated pressure for a microcalorimeter based on DSC principles. David¹¹ determined K as a function of N_2 or He pressure (at constant temperature) or as a function of temperature (at constant elevated pressure). Unfortunately, the K values determined by David were calculated on the basis of the heat of melting of standard materials at atmospheric pressure without corrections for pressure change, which introduced some uncertainty in the results.

Although DuPont elevated pressure DSC has been used for a variety of applications,^{6,7} quantitative determinations of ΔH and K values at elevated pressures have not been reported. According to Levy et al.,⁶ K varies less than 10% over the 10 μm to 1000 psi pressure and -190°C to 650°C temperature ranges; still the calibration coefficient should be determined for the pressure range used. Moreover, in DuPont DSC, K or W values are not independent of temperature. W or K , therefore, must be calibrated against standard materials which have melting temperatures within the temperature interval of interest.

As described in our previous paper,³ the DSC curves for hydrogen peroxide run in hermetically closed plain aluminum pans provided with a pinhole for pressure equilibration under 975 psi N_2 pressure yield an exotherm peaking at 187°C . This exotherm corresponds to the decomposition of hydrogen peroxide. The DSC curves of hydrogen-peroxide-treated lignocellulose under the same environmental conditions yield two exothermic peaks at $135\text{--}180^\circ\text{C}$ and at $200\text{--}235^\circ\text{C}$, respectively, depending on the type of wood component; a change to O_2 environment increases drastically the $200\text{--}235^\circ\text{C}$ exotherms. Represen-

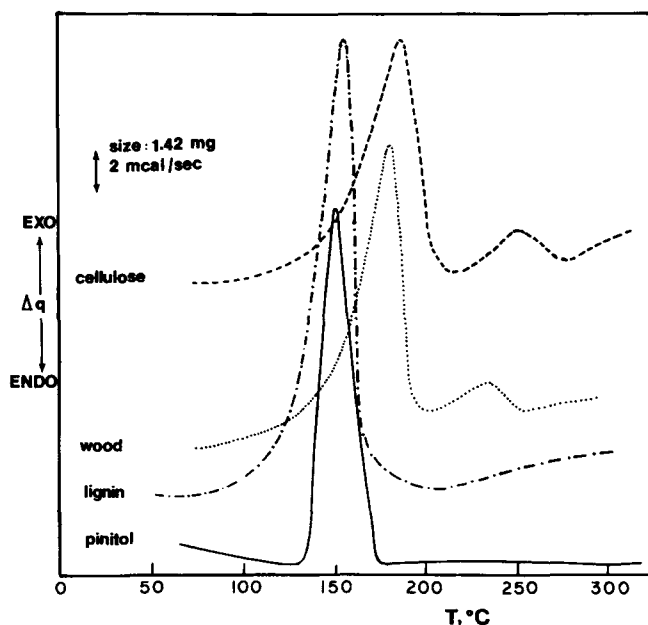


Fig. 1. DSC of H_2O_2 -treated lignocellulose in N_2 ; hermetically sealed plain aluminum pan provided with a pinhole; heating rate = $20^\circ\text{C}/\text{min}$; pressure = 975 psi (Pinitol = 5-*O*-methyl *d*-inositol).

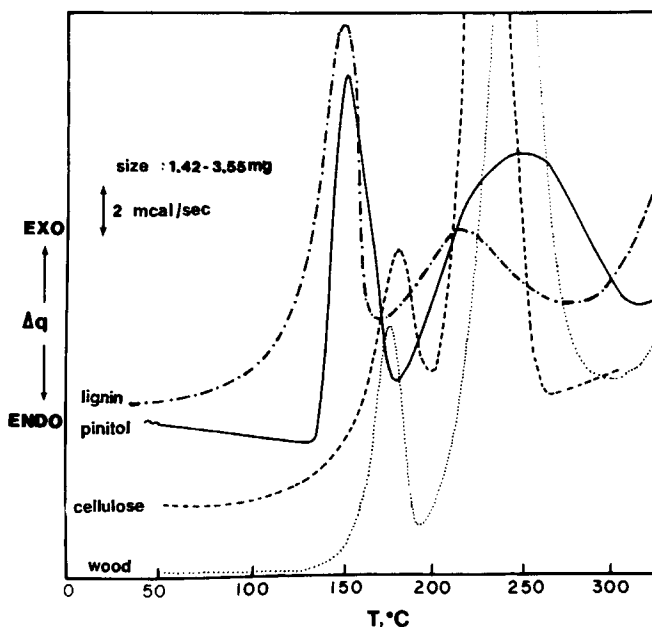


Fig. 2. DSC of H_2O_2 -treated lignocellulose in O_2 . Conditions are as in Figure 1.

tative DSC curves of H_2O_2 -treated lignocellulosic materials at 975 psi are given in Figures 1 and 2. In order to calculate the enthalpies of the reactions, W values were evaluated as a function of pressure utilizing as standard materials indium (In), tin (Sn), and zinc (Zn). The heat of fusion ΔH_{f0} and the melting point T_m at atmospheric pressure for indium, tin, and zinc are 6.8 cal/g and 156.3°C, 14.4 cal/g and 231.7°C, and 24.4 cal/g, and 419.4°C, respectively.¹⁹

Calibration Coefficient W

The cell calibration coefficient at a given pressure (W_p) is calculated from the temperature scan using the following expression:

$$W_p = \frac{\Delta H_{fp} \times m \times 6.452}{A_p \times B \times \Delta q} \quad (4)$$

where ΔH_{fp} is the heat of melting of the standard material (indium, tin, or zinc) at a given pressure and A_p is the peak area of the standard material at a given pressure. Other symbols are described above.

The values for ΔH_{fp} of the standard materials, indium, tin, and zinc, were calculated for different pressures using the formula

$$\Delta H_{fp} = \frac{\Delta H_{f0}}{T_{m0}} \times T_{mp} \quad (5)$$

where ΔH_{f0} and T_{m0} are the heat of fusion and melting point at atmospheric pressure and ΔH_{fp} and T_{mp} are the heat of fusion and melting point at a particular pressure of interest, respectively. The applicability of (5) for calculation of ΔH_{fp} of indium in the pressure range of 0–50 kbar has been demonstrated by

Kutasov.²⁰ Equation (5) is based on the assumption of a negligible change in entropy of fusion, ΔS_f , with pressure. It is well known that the entropy of fusion of materials composed of atom particles such as metals is small and reasonably constant, about 2 eu/mol.²¹ Furthermore, the work of Stishov²² indicates that the decrease in entropy of fusion of aluminum and copper observed between zero and 5×10^5 bar is negligible within our present range. On the basis of all the above, we assumed the applicability of (5) for calculation of ΔH_{fp} of zinc and tin, too.

Combining eq. (4) with eq. (5), we obtain an expression for W_p :

$$W_p = \frac{6.452m(\Delta H_{f0}/T_{m0})T_{mp}}{A_p B \Delta q} \quad (6)$$

Determining T_{mp} and A_p for the standard materials, In, Sn, and Zn, in the pressure range of interest permitted the determination of W_p for the DuPont DSC used in this study.

Kinetic Parameters

During the last two decades, a considerable number of kinetic methods of analysis were developed for nonisothermal reactions based on DSC curves.²³⁻²⁶ These methods were derived assuming that the kinetic equations for isothermal homogeneous gas or liquid could be applied.

Four methods for obtaining kinetic parameters directly from DSC are available at the present time: the Kissinger method²⁷ and the Ozawa method,²⁸ which are based on the correlation between heating rate and peak temperature T_p , the Rogers and Morris method,²⁹ which is based on the distances between the reaction curve and the base line, and the modified Borchardt and Daniels method,³⁰ which assumes that the heat evolved is directly proportional to the number of moles reacted.

Numerous attempts have been made to use these methods to determine kinetic parameters associated with a variety of chemical reactions. For example, Kissinger's method has been used to determine the activation energy associated with the oxidation reaction of rubber^{31,32} and oxidative thermal degradation of plastics.³³ Ozawa's method has been used in studies of industrial materials, particularly in high polymer research,^{28,34} while Rogers and Morris's method and the modified method of Borchardt and Daniels have been used to study the kinetics of explosive reactions²⁹ and decomposition of polymerization initiators,³⁰ respectively. In the present study, Ozawa's method was solely used as it is the most straightforward and applicable to most materials.³⁴ Also, Ozawa's method can be used without making assumptions about reaction order.

The theoretical basis of Ozawa's method is derived from the general form of the isothermal reaction kinetics equation:

$$\frac{dx}{dt} = Z e^{-E/RT} G(x) \quad (7)$$

where x = degree of conversion at time t , T = the absolute temperature, Z = the Arrhenius frequency factor, E = the activation energy, R = the gas constant, and $G(x)$ = a function of the composition of the system. The integral form (8), which

relates the heating rate β and peak temperature T_p , is an approximate formulation derived from [7].

$$\frac{d \log \beta}{d(1/T_p)} = -0.457 \frac{E}{R} \quad (8)$$

According to this equation, E , the activation energy of reaction, can be estimated from the plot of the logarithm of the heating rate against the reciprocal absolute temperatures of the peaks. This is called Ozawa's plot. Although Ozawa's method was developed for thermogravimetry, it is applicable to DSC. The DuPont DSC is well suited for this kinetic method due to its linear heating rates and ability to directly record the sample temperature via a thermal sensor located in the vicinity of the sample.

Using the value of E obtained by Ozawa's method, we can obtain approximate values for other kinetic parameters. For a first-order reaction, Z , the Arrhenius frequency factor, is calculated using eq. (9):

$$Z = \frac{\beta E e^{-E/RT_p}}{RT_p^2} \quad (9)$$

where β and T_p represent their values at the middle of the range of the heating rates used. The rate constant k can be obtained from the Arrhenius equation:

$$k = Z e^{-E/RT} \quad (10)$$

Kinetic parameters were assumed not to change with pressure.

MATERIALS AND EXPERIMENTAL PROCEDURES

The procedures used in this work have been described in a previous paper.³ The standard samples of In, Sn, and Zn were Baker reagent grade chemicals obtained from DuPont, which have a purity of 99.9%. The standard samples were run in a hermetically sealed plain aluminum pan provided with a pinhole under N₂ pressures of 14.7, 175, 450, 650, and 975 psi, at a heating rate of 10°C/min with the same standard sample used for all pressures. The pressure was allowed to stabilize for 10 min before each run. The starting temperature was 30°C below that of the melting point. Because the melting point was to be obtained, the temperature scan was used. Peak area was determined by the weighing method, using a Cahn microbalance. The melting point T_m —the intersection of the leading edge of the endotherm and the base line—was taken from the corrected chart (20°C/in. for In; 50°C/in. for Sn and Zn). For purposes of comparison, this method is considered sound, though not the most accurate. All the T_m results are reported as the average of four measurements at each pressure except for In at ambient pressure, where six measurements were averaged. For zinc at 975 psi, correction was made for the fact that the starting temperature lagged 5.5°C behind the chart temperature. For T_m determinations, the instrument settings were $\Delta q = 0.787$ mcal/s-cm and $B = 47.22$ s/cm for In and $\Delta q = 0.787$ mcal/s-cm and $B = 59.04$ s/cm for Sn and Zn. Our source of lignocellulosic materials and methods of sample preparation are described in an earlier paper.³ The refined brown-rot of *Libocedrus decurrens* was used as lignin; microcrystalline commercial Sigmacell Type 38 cellulose was used as

cellulose; 60–80 mesh extractive-free *Abies concolor* wood powder was used as wood; glucose was obtained from Eastman Org. Chem., and pinitol (a cyclitol, 5-*O*-methyl *D*-inositol) was prepared from *Pinus lambertiana* wood extract. Unless stated otherwise, all H_2O_2 and H_2O_2 -treated lignocellulose samples were run in a hermetically sealed plain aluminum pan provided with a pinhole at 975 psi N_2 pressure and at $20^\circ C/min$ heating rate. For determination of kinetic parameters, five different heating rates were used (2, 5, 10, 20 and $50^\circ C/min$). The slope was obtained from Ozawa's plot by the least squares method, while the E value was calculated from eq. (8) without further refinement. The characteristic DSC run for various materials used in N_2 and O_2 are reproduced in Figures 1 and 2.

RESULTS AND DISCUSSION

Calibration Coefficient and Heat of Reaction

Figures 3, 4, and 5 show the dependence of specific melting peak area (A/m in cm^2/mg), melting enthalpy (ΔH_{fp} in cal/g) of the standard materials, and DuPont cell calibration coefficient W , respectively, on N_2 pressure. ΔH_{fp} and W_p were calculated using eqs. (4) and (5), respectively. The results show that, although the dependence on pressure of the properties examined was small, a

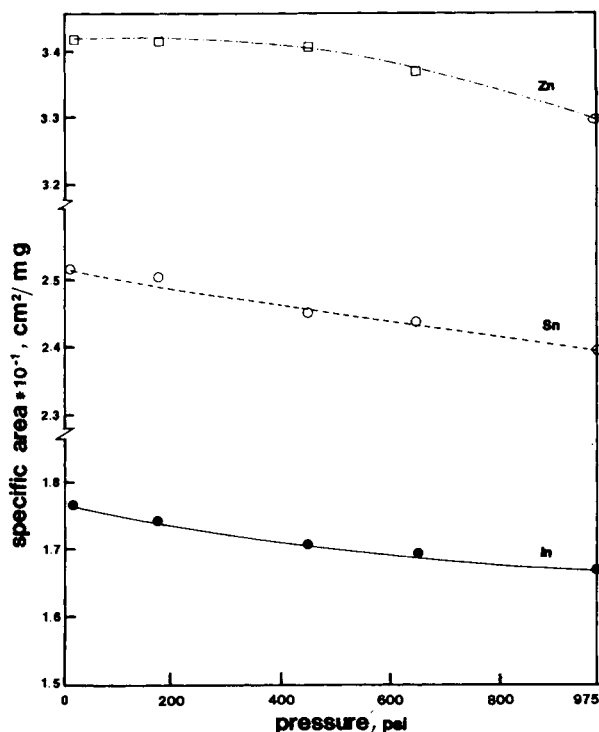


Fig. 3. Dependence of the specific peak area of melting (A/m) on N_2 pressure for Zn, Sn, and In.

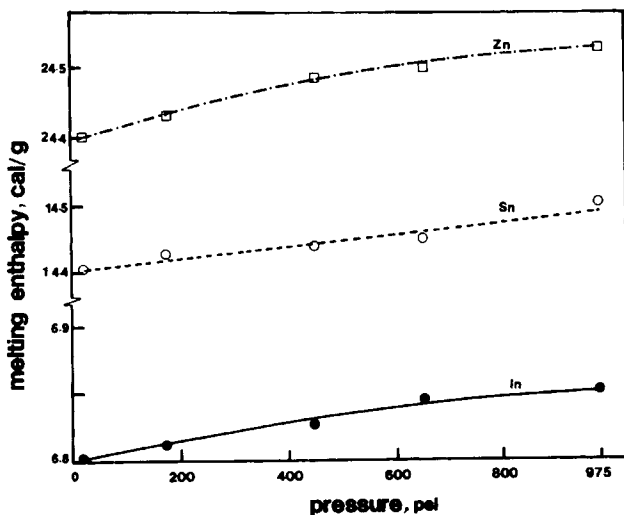


Fig. 4. Dependence of the melting enthalpy of Zn, Sn, and In on pressure.

definite trend was evident. With increasing pressure peak area decreased, whereas the melting enthalpy, melting point, and cell calibration coefficient W increased. Considerable variation in the cell calibration coefficient with respect to temperature is observed in Figure 6, where the coefficient was plotted against the recorded melting points of In, Sn, and Zn at three different pressures.

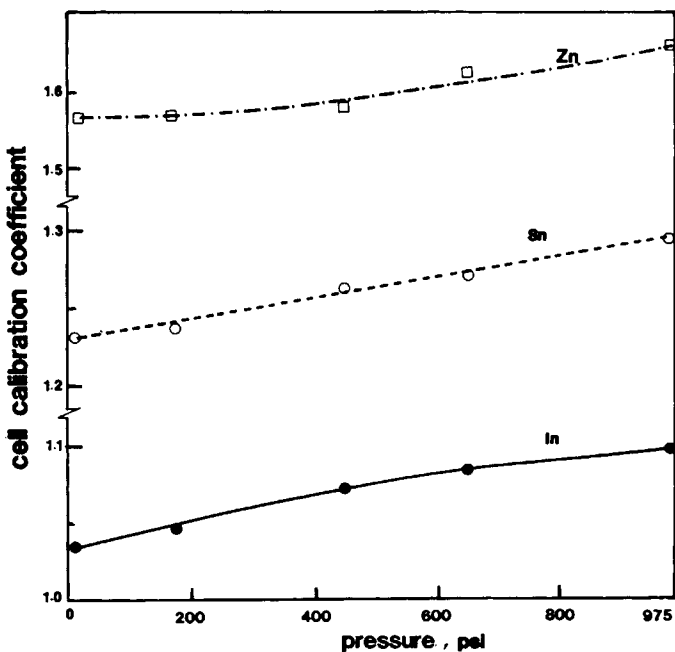


Fig. 5. Dependence of the cell calibration coefficient W on pressure determined for the melting of Zn, Sn and In.

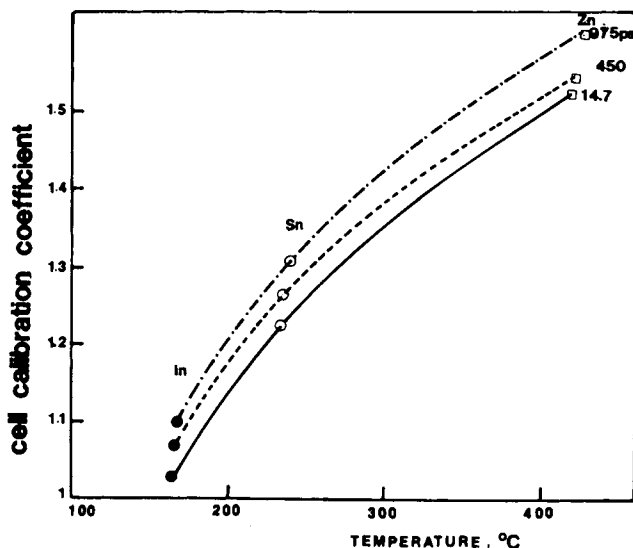


Fig. 6. Relationship between cell calibration coefficient *W* and temperature.

Heat of H₂O₂ decomposition and heat of reaction between H₂O₂ and lignocellulosic materials at 975 psi were calculated using eq. (3) and using *W* values obtained for In (*W* = 1.098) and Sn (*W* = 1.296). These results are presented in Table I.

TABLE I
Enthalpy of Hydrogen Peroxide Decomposition and Reaction between Hydrogen Peroxide and Lignocellulosic Materials in N₂ and O₂ at 975 psi Pressure

Materials	ΔH_1 Total enthalpy of 1st peak (cal/g H ₂ O ₂)	ΔH_2 Enthalpy of 2nd peak (cal/g carbohyd)
<i>In Nitrogen</i>		
H ₂ O ₂	720	—
<i>H₂O₂-treated</i>		
Lignin	2500	—
Wood	1940	170 ^a
Cellulose	1840	128
Arabinoxylan	1930	417
Pinitol	1670	—
Glucose	1860	228
<i>In Oxygen</i>		
H ₂ O ₂	687	—
<i>H₂O₂-treated</i>		
Lignin	2020	528 ^b
Wood	1490	2030 ^a
Cellulose	1450	2830
Pinitol	1630	489
Glucose	1510	1640

^a Assuming 75% of white fir is carbohydrate.

^b Based on 100% lignin.

The value for the heat of decomposition for hydrogen peroxide (50 wt %) obtained in this study at 975 psi and 187°C (720 cal/g H₂O₂) is somewhat higher than the value of 670 cal/g H₂O₂ obtained at ambient pressure and 25°C by Giguère.³⁵ The difference is most likely due to the different temperature and pressure conditions used in those experiments.

It is interesting to note that the reaction between lignin and hydrogen peroxide in nitrogen yields the highest enthalpy among the wood components examined. Wood and hemicellulose yield surprisingly similar heats of reaction with hydrogen peroxide in both N₂ and O₂. Similar heats of reaction were also obtained for the reactions of cellulose or glucose with hydrogen peroxide. The results also indicate that heats of reaction are considerably higher in N₂ than in oxygen atmosphere, and that, with the exception of pinitol, the differences in heat of reaction between reactants run in oxygen are similar to the differences obtained in nitrogen.

In the second exothermic reaction(s) (oxidation of lignocellulose and related materials by oxygen), the enthalpies were much higher in O₂ than in N₂ atmosphere. For N₂, the exothermic reactions of H₂O₂-treated hemicellulose (xylan) yielded the highest enthalpy, while cellulose, lignin, and pinitol yielded the lowest enthalpies. In fact, no second exotherm was observed for H₂O₂-treated lignin or pinitol in N₂, whereas large enthalpies were associated with the second exotherm of H₂O₂-treated lignin or pinitol in O₂ atmosphere. Similar results were obtained for H₂O₂-treated cellulose, glucose, and wood. The enthalpies in O₂ were 22, 12, and 7 times greater than those measured in N₂ for cellulose, wood, and glucose, respectively. In N₂ atmosphere the second exotherm apparently results from the reaction of carbohydrates with O₂ derived as the byproduct of the first exothermic reaction and/or with entrapped O₂. Where much greater quantities of O₂ are available (e.g., in O₂ atmosphere), the reaction results in the evolution of considerably greater quantities of heat.

Kinetic Parameters

Ozawa's plot of 50 wt % hydrogen peroxide, hydrogen-peroxide-treated wood, cellulose, and lignin in N₂ are shown in Figure 7. Activation energy values and Arrhenius frequency factors in both nitrogen and oxygen are presented in Table II. Except for the *E* value of hydrogen peroxide in O₂, which is considerably lower than that in nitrogen, activation energies are very similar considering the approximations used and experimental errors. For hydrogen peroxide (50 wt %) the rate constants for hydrogen peroxide decomposition at 160°C were independent of atmospheric composition with $t_{1/2} = 2.07$ min in N₂ and $t_{1/2} = 1.92$ min in O₂.

Considerable variations in the kinetic parameters (*E*, *k*₂, and *t*_{1/2}) for hydrogen peroxide decomposition have been reported in the literature because of the extraordinary sensitivity of hydrogen peroxide decomposition to slight changes in the physical nature of the reaction container, pH, pressure, temperature, concentration, or surface-to-volume ratio. Baker and Ouellet³⁶ reported apparent activation energies for decomposition of hydrogen peroxide vapor varying between 13.4 and 19.0 kcal/mol as a function of the nature of a glass surface at 10–20 mm Hg pressure and 70°C to 200°C. They showed that the rate of hydrogen peroxide decomposition was faster in lime-soda glass than in ordinary

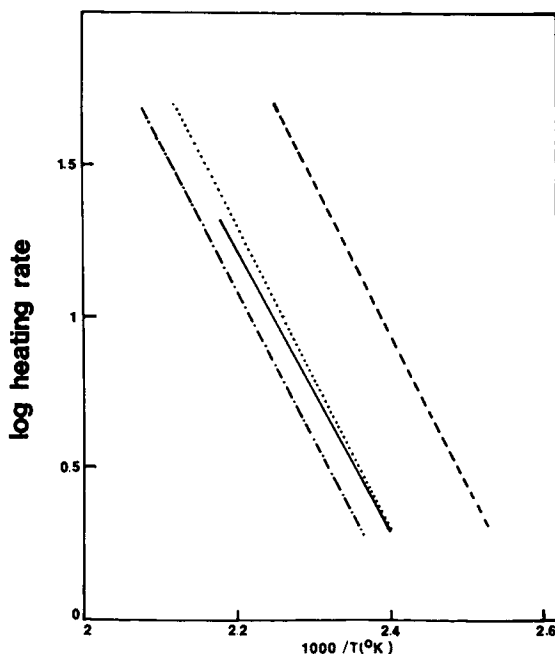


Fig. 7. Relationship between logarithm of the heating rate and reciprocal absolute temperature (Ozawa's plot) as determined for H_2O_2 and H_2O_2 -treated wood, cellulose, and lignin, in N_2 . The curves follow in all cases the values determined, which were omitted for clarity: (—) H_2O_2 ; (- · - ·) cellulose; (· · ·) wood; (- - -) lignin.

pyrex, and faster in ordinary pyrex than in fused pyrex. Giguère³⁵ reported similar results, assuming H_2O_2 vapor decomposition to be a first-order reaction. His E values for H_2O_2 vapor decomposition at 5 mm Hg ranged between 8.0 and 21.6 kcal/mol, while soda-lime glass yielded an activation energy of 11.4 kcal/mole. It has been found that the nature of the surface produces a significant effect on the kinetics of H_2O_2 decomposition in the liquid as well as in the vapor phase.³⁷ Thus, due to the considerable variability of reported values for E , k , and $t_{1/2}$ resulting from differences in experimental conditions, it is not possible to compare directly the kinetic results of this study with those of previous reports.

TABLE II
Kinetic Parameters of H_2O_2 and the First Exothermic Peak of H_2O_2 -Treated Lignocellulose in O_2 and N_2 , Determined by Ozawa's Method

Materials	N_2			O_2		
	Activation energy E (kcal/mol)	Frequency factor Z (min^{-1})	Rate constant at 160°C , k (min^{-1})	Activation energy E (cal/mol)	Frequency factor Z (min^{-1})	Rate constant at 160°C k (min^{-1})
H_2O_2	20.3	5.70×10^9	0.334	15.9	3.73×10^7	0.361
H_2O_2 -treated						
Cellulose	21.9	2.71×10^{10}		21.7	3.36×10^{10}	
Lignin	21.3	6.59×10^{10}		22.4	2.23×10^{11}	
Wood	22.1	4.50×10^{10}		19.7	2.77×10^9	

References

1. T. Ozawa, *Thermal Anal.*, **9**, 217 (1976).
2. T. Nguyen, E. Zavarin, and E. M. Barrall, II, *Thermochim. Acta*, **41**, 107 (1980).
3. T. Nguyen, E. Zavarin, and E. M. Barrall, II, *Thermochim. Acta*, **41**, 269 (1980).
4. T. Nguyen, E. Zavarin, and E. M. Barrall, II, *J. Appl. Polym. Sci.*, **27**, 1019 (1982).
5. J. Sestak, V. Satawa, and W. W. Wendlandt, *Thermochim. Acta*, **7**, 333 (1973).
6. P. F. Levy, G. Nieuweboer, and L. C. Semanski, *Thermochim. Acta*, **1**, 429 (1970).
7. W. E. Collins, *Anal. Calorimetry*, **2**, 353 (1970).
8. D. J. David, *Anal. Chem.*, **37**, 82 (1965).
9. J. F. Johnson, *Thermochim. Acta*, **1**, 373 (1970).
10. J. R. Williams and W. W. Wendlandt, *Thermochim. Acta*, **7**, 273 (1973).
11. D. J. David, in *Analytical Calorimetry*, R. S. Porter and J. M. Johnson, Eds., Plenum, New York, 1970, Vol. 2, pp. 369-387.
12. M. Kamphausen, *Rev. Sci. Instrum.*, **46**, 668 (1975).
13. M. Kamphausen and M. Schneider, *Thermochim. Acta*, **22**, 371 (1978).
14. K. Takamizawa, T. Takemura, T. Oyama, H. Uchida, K. Toshima, and N. Miyamoto, *The Eleventh Japanese Calorimetry Conference*, Fukuoka, abstract paper, 1975, p. 15.
15. K. Takamizawa, *Thermochim. Acta*, **25**, 1 (1978).
16. P. W. Bridgman, *The Physics of High Pressure*, Bell, London, 1949, pp. 189-222.
17. P. W. Bridgman, *Phys. Rev.*, **48**, 893 (1935).
18. A. Wurfliinger and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, **77**, 121 (1973).
19. *Handbook of Chemistry and Physics*, 53rd ed., The Chemical Rubber Co., 1972-1973, pp. B-241, B-244.
20. I. M. Kutasov, *Phys. Solid Earth*, **44** (1974).
21. G. W. Castellan, *Physical Chemistry*, 2nd ed., Addison-Wesley, Reading, Mass., 1971, pp. 178, 89, 186.
22. S. M. Stishov, *Sov. Phys. Usp.*, **11**, 816 (1969).
23. E. P. Manche and B. Carroll, in *Physical Methods in Macromolecular Chemistry*, B. Carroll, Ed., Marcel Dekker, New York, 1972, Vol. 2, p. 239.
24. W. W. Wendlandt, *Thermal Methods of Analysis*, 2nd ed., Wiley-Interscience, New York, 1974, pp. 187-192.
25. E. M. Barrall, II, and J. F. Johnson, in *Techniques and Methods of Polymer Evaluation*, D. E. Slade and L. T. Jenkins, Eds., Marcel Dekker, New York, 1970, pp. 1-39.
26. H. M. Hauser and J. E. Field, *Thermochim. Acta*, **27**, 1 (1978).
27. H. E. Kissinger, *Anal. Chem.*, **29**, 1072 (1957).
28. T. Ozawa, *J. Thermal Anal.*, **2**, 301 (1970).
29. R. N. Rogers and E. D. Morris, Jr., *Anal. Chem.*, **38**, 412 (1966).
30. K. E. J. Barrett, *J. Appl. Polym. Sci.*, **11**, 1617 (1967).
31. S. H. Goh, *J. Elastomers Plast.*, **9**, 186 (1977).
32. S. H. Goh and K. W. Phang, *Thermochim. Acta*, **25**, 109 (1978).
33. T. Kotoyori, *Thermochim. Acta*, **5**, 51 (1972).
34. A. A. Duswalt, *Thermochim. Acta*, **8**, 57 (1974).
35. P. A. Giguère, *Can. J. Res.*, **B25**, 135 (1947).
36. B. E. Baker and C. Ouellet, *Can. J. Res.*, **B23**, 167 (1945).
37. W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, ACS Monograph Ser. No. 128, Reinhold, New York, 1955, p. 456.

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