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ON THE USE OF THE ARRHENIUS EQUATION TO DESCRIBE CELLULOSE AND WOOD PYROLYSIS

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ABSTRACT

The Arrhenius equation has been succesfully used in chemical reaction kinetics to describe the temperature dependence of the reaction rate constant. However, in a recent communication, D.J. Brown suggested that application of the Arrhenius equation in cellulose and wood pyrolysis studies is inappropriate. Based on results from isothermal pyrolysis studies in which heat and mass transfer effects were negligible, it has been shown that the Arrhenius equation adequately describes the temperature dependence of the overall degradation rate constant for cellulose and wood pyrolysis. Although the Arrhenius equation has little physical significance in solid-state reactions, it may be assumed as a two-parameter model to correlate the data thereby minimizing the number of adjustable parameters.

INTRODUCTION

In many chemical reactions, the temperature dependence of the reaction rate constant has been found to be well represented by the Arrhenius equation

$$k = A\exp(-E/RT) \tag{1}$$

where k is the reaction rate constant, A is the frequency factor or the pre-exponential factor, and E is the activation energy or the apparent activation energy. It may be recalled that $\exp(-E/RT)$ is a Boltzmann distribution function for the fraction of molecules having an energy E in excess of the average energy. The success of this empirical Arrhenius equation to correlate the data has led to the development of collision and transition state theories, thereby enhancing our knowledge of the mechanisms involved in the transformation of reactants into products.

It should be emphasized that the Arrhenius law applies only to a simple homogeneous gas-phase reacting system. In many cases complex reactions appear to follow a simple kinetic order over a range of limited experimental conditions. In other systems, a relation between ln k and $1/T$ is nonlinear. This nonlinearity may suggest a change in reaction mechanism or that the

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reacting system may have become physically limited due to heat and mass transfer effects. Some reasons for nonlinearity between ln k and $1/T$ in some biomass pyrolysis studies are: complexity of the reaction, possible errors in sample temperature measurement [1–3], and temperature gradient within the sample (heat and mass transfer effects).

In a recent communication, Brown [4] suggests that the application of the Arrhenius equation may be inappropriate in cellulose and wood pyrolysis studies. In fact, the Arrhenius equation has been reported to be unsuitable for some thermoanalytical studies [5]. Arnold et al. [5–7] have suggested that dynamic thermoanalytical curves provide insufficient information for the accurate estimation of Arrhenius parameters. Manipulation of "frequency factor", "activation energy", and "order of reaction" to fit the data to a single curve results in a nonunique solution between the estimated parameters and the measured curves [6].

Despite these studies [4,5], the Arrhenius equation has been extensively used in biomass pyrolysis studies to describe the temperature dependence of the degradation rate constant [1,3,8–14]. Since the publication of the review by Roberts [14], significant progress has been made in understanding the kinetics and mechanisms involved in the pyrolysis of cellulosic materials [3,12,13]. Brown's [4] objection to the use of the Arrhenius equation to describe the pyrolysis kinetics of cellulose and wood seriously undermines these efforts. In this communication, an attempt is made to understand the role of the Arrhenius equation in the pyrolysis of cellulosic materials.

DISCUSSION

Based on the results reviewed by Roberts [14], Brown [4] suggests that the Arrhenius equation is unsuitable in cellulose and wood pyrolysis studies. Brown's major objection is the appearance of a compensation effect [8,9] (linear relation between E and log A) in the pyrolysis of cellulose and wood. Brown [4] suggests that a relation between E and log A is due to the application of the Arrhenius equation mistakenly under conditions where another relationship should have been used (e.g., heat transfer controlled reactions). Table 1 summarizes the Arrhenius parameters reviewed by Roberts [14]. Linear statistical analysis for a relationship between ln A and E suggests the following relationship

$$\ln A = 11.67(\pm 14.18) + 0.12(\pm 0.10)E$$

with a correlation coefficient of 0.65. The figures in parentheses represent error limits for the estimated values at 95% confidence. A low correlation coefficient and high error limits suggest no linear relationship between E and ln A in this data set. Hence, existence of the compensation effect between "groups" of results to establish the mechanism governing the pyrolysis reaction is misleading.

TABLE 1

Summary of Arrhenius parameters reviewed by Roberts [14]

E(kJ mol^{-1})	A(min^{-1})	Authors/remarks
Substrate: cellulose		
146.4	3.85×10^{11}	Tang (1st Stage)
103.7	-	Akita (270–340°C)
108.6	2.88×10^{11}	Stamm (110–220°C)
134.3	7.80×10^{13}	Kujirai and Akahira (165–265°C)
209.0	–	Madorsky et al. (275–305°C)
175.6	2.28×10^{16}	Lipska and Parker (250–300°C)
234.3	2.37×10^{19}	Tang (final stage)
Substrate: wood		
104.6	2.60×10^{9}	Roberts and Clough (< 300°C)
94.6	2.65×10^{8}	Murty and Blackshear ($r/a = 0.86$)
124.7	3.6×10^{9}–4.5×10^{10}	Tinney (upper limits)
87.7	2.09×10^{17}	Murty and Blackshear ($r/a = 1.0$)
62.8	5.46×10^{6}	Roberts and Clough ($T > 300$°C)
152.3–178.6	2.4×10^{10}–1.2×10^{11}	Tinney (lower limits)
138.7	3.18×10^{10}	Bamford et al. (297–447°C)

As an alternative to use of the Arrhenius equation, Brown [4] gives an example whereby it is assumed that there is heat transfer control of the reaction rate constant of the form

$$k = C(T - T_0) \tag{2}$$

where C is a constant, T_0 the sample temperature and T the wall temperature. Using a value of $T_0 = 673$ K and $C = 0.2$, he found a nonlinear relation between log k and inverse temperature over the temperature range 678–773 K. The nonlinear behavior was claimed due to inappropriate use of the Arrhenius equation. It should be noted that eqn. (2) represents k as a linear function of temperature. Hence, log k as an inverse function of temperature will be nonlinear in most cases over a wide range of temperature. Therefore, the use of heat transfer control of reaction rate constant k as described by eqn. (2), to question the validity of the Arrhenius equation, is incorrect.

If a process is heat transfer limited, then the energy balance in a differential control volume for constant effective thermal is [15]

$$\frac{\partial}{\partial t}(C_p \rho T) = K\left(\frac{\partial^2 T}{\partial r^2} + \frac{b-1}{r}\frac{\partial T}{\partial r}\right) + (-q)\left(-\frac{\partial \rho}{\partial t}\right) \tag{3}$$

where C_p, ρ, K are the solid specific heat capacity, density, and effective thermal conductivity, respectively. q is the apparent enthalpy change associated with the set of chemical and physical changes, T is the local temperature, r is the radial position, and b is a geometrical factor. This equation represents a modification of the Bamford et al. [16] model which combined the equation for heat conduction on pyrolyzing a solid with those for heat generation. Since pyrolysis reactions are complex and involve both endothermic and exothermic processes, the energy equation obtained from a shell balance can be further simplified to characterize the rate limiting process, namely: external transfer control (uniform internal conditions), internal transfer control (uniform external control), and kinetic control (uniform external and internal conditions). For a detailed description of the heat transfer process involved in pyrolysis, an interested reader is referred to the literature [15–21]. The goal of this paper is limited to the kinetically controlled regime (free of heat and mass transfer limitations) where the Arrhenius equation is applicable.

For the pyrolysis of biomass, the rate of weight loss may be taken as proportional to either the amount of future weight loss, the amount of sample residue, or the amount of remaining substrate. For char, tar and gas formation occurring through independent, homogeneous, first-order reactions, the rate equations for the weight loss may be obtained from mass balance as [3]

$$\frac{dW_s}{d\theta} = -\left(k_g + k_t + k_c\right)W_s = -kW_s \tag{4}$$

$$\frac{dW_c}{d\theta} = k_c W_s \tag{5}$$

where W is weight, θ is time, k is a rate constant, and subscripts s, t, c, and g refer to substrate, tar, char, and gas, respectively. The rate of weight loss may be represented by the sum of eqns. (4) and (5). These equations can be integrated subject to the initial condition that when isothermal conditions are first achieved, the amount of substrate is W_s^0, the amount of char formed during the heat-up period is W_c^0, etc. The weight of substate and char as a function of time are, thus

$$W_s = W_s^0\,e^{-k\theta} \tag{6}$$

$$W_c = W_c^0 + W_s^0\frac{k_c}{k}(1 - e^{-k\theta}) \tag{7}$$

where $\theta = 0$ is the time of attainment of isothermal conditions. Equation (7) may be rewritten as

$$R - R_\infty = W_s^0(1 - k_c/k)\,e^{-k\theta} \tag{8}$$

where R is the sum of weights of unreacted substrate, char, and ash. R_∞ is the weight of residue after "infinite time". Equation (8) suggests that a plot of $\ln(R - R_\infty)$ versus time should be a straight line whose slope is equal to the negative value of the overall degradation rate constant k. k may be assumed to follow an Arrhenius temperature dependence represented by eqn. (1).

To justify the applicability of the Arrhenius equation, isothermal studies,

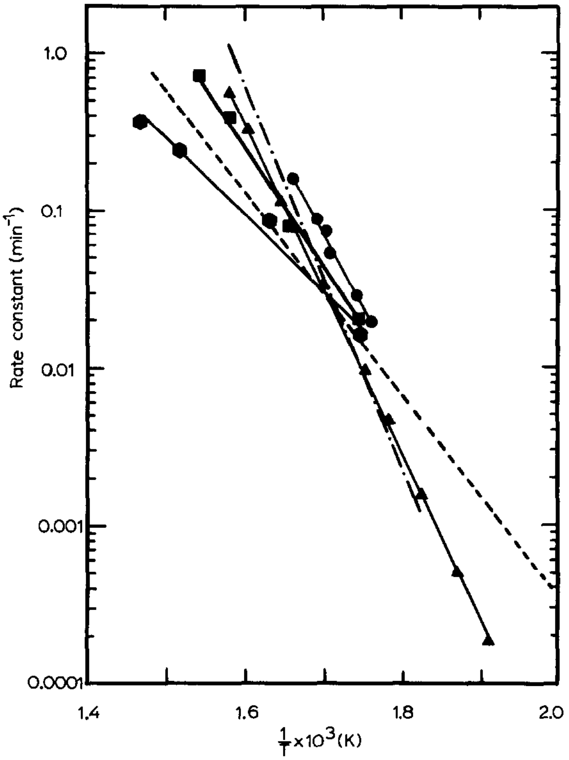

Fig. 1. Arrhenius plot for the isothermal pyrolysis of cellulose and wood: (●) data of Bradbury et al. [24] for cellulose pyrolysis; (▲) data of Lipska et al. [22,23] for cellulose pyrolysis; (■) data of Agrawal [3] for cellulose pyrolysis; (⬢) data of Agrawal for wood pyrolysis; (- - - -) group I ($A = 4.2\times10^9$ min^{-1}, $E = 125.5$ kJ mol^{-1}); (–·–·–) group II ($A = 2.4\times10^{19}$ min^{-1}, $E = 234.3$ kJ mol^{-1}) for pyrolysis of small cellulose samples as suggested by Roberts [14].

where sample temperatures were measured, have been chosen. Experimental conditions used in isothermal pyrolysis studies of Agrawal [3], Lipska et al. [22,23], and Bradbury et al. [24], suggest that heat and mass transfer effects in their system are negligible. Figure 1 represents the Arrhenius plots for the overall degradation rate constant obtained in these studies. Table 2 sum-

TABLE 2

Arrhenius parameters from isothermal pyrolysis studies

Substrate	A(min^{-1})	E(kJ mol^{-1})	Correlation coefficient	Ref.
Cellulose	1.03×10^{12}	150.7	0.994	Agrawal [3]
Cellulose	2.27×10^{16}	201.1	0.999	Lipska et al. [22,23]
Cellulose	1.27×10^{15}	182.8	0.995	Bradbury et al. [24]
Wood	4.78×10^{6}	92.2	0.981	Agrawal [3]

marizes the results obtained from linear least-squares regression analysis. Arrhenius parameters suggested by Roberts [14] to describe small cellulose samples are also shown in Fig. 1 for comparison. The plot is linear suggesting that the Arrhenius type equation is helpful in modeling cellulose and wood pyrolysis reaction kinetics. The parameters thus derived can predict the weight loss and product formation kinetics [3]. Hence, it is seen that an Arrhenius type equation is helpful in correlating the pyrolysis data.

Although the Arrhenius equation has little physical significance in solid-state reactions, it may be assumed as a two-parameter model. The validity of Arrhenius type equations in numerous studies and in various fields suggests that the Arrhenius equation can be a powerful tool to correlate data, and minimize the number of adjustable parameters in fitting the data. Nonlinearity in the Arrhenius equation may indicate a change in reaction mechanism or that the reaction system has become physically limited due to heat and mass transfer effects.

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