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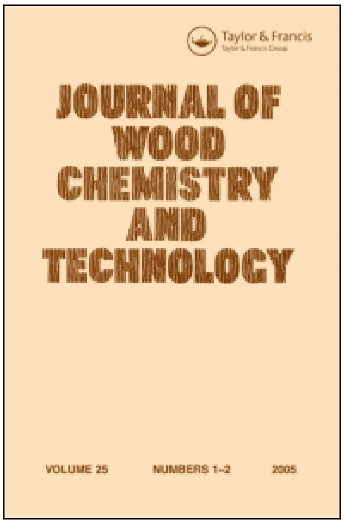

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A CHEMICAL KINETICS STUDY OF THE PROPIONIC ANHYDRIDE MODIFICATION OF CORSICAN PINE. (1):DETERMINATION OF ACTIVATION ENERGIES.

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ABSTRACT

The chemical kinetics of wood modification using propionic anhydride with pyridine as solvent/catalyst have been investigated. Reactions at the surface obey pseudo first-order kinetics, by determining rate constants for the reaction at a series of temperatures the activation energy for the surface reactions has been obtained. A comparison of the use of methods of rate constants and initial rates to determine activation energies has shown that the two methods give different values of E_a. It is thought that this discrepancy can be attributed to the change in the number of surface reactive sites with temperature.

INTRODUCTION

Although the literature relating to carboxylic acid anhydride-wood modification reactions is extensive[1,2,3], there has been no study reported in the scientific literature on the kinetics of the reaction. This information is of fundamental importance when considering such issues as mechanism of reaction, or designing efficient large scale processes. Wood represents an exceedingly complex substrate upon which to perform chemical reactions, and the kinetics would be expected to reflect this complexity. Apart from the difference in reactivities of the hydroxyl functionalities associated with the various chemical constituents of wood, variations in behaviour can be expected due to location of site (surface, bulk etc.) and the immediate stereochemical environment associated with each site. The following argument applies to a reaction where wood blocks are pre-swollen in a suitable solvent before reagent is added. Viewed simplistically, taking no account of the different chemical species, the wood anhydride reaction can be represented as shown in figure 1. The rate expression for such a chemical reaction scheme is as follows:

$$\frac{d[OH]}{dt} = -k\,[OH]\,[anhyd] \qquad (1)$$

Where [OH] is the concentration of hydroxyl groups and [anhyd] the concentration of anhydride reagent. In a conventional homogeneous chemical reaction, the two reagents are dispersed throughout the solvent evenly. When performing the reactions on wood blocks, the hydroxyl groups are located in a small volume within the solution. Furthermore, during the initial stages of the reaction it is reasonable to assume that the 'surface' sites will dominate the kinetics. Therefore, initially, the change in concentration of anhydride reagent will be very small and it is legitimate to write $[Anhyd]_0 = [Anhyd]_t$, where $[Anhyd]_0$ is the concentration of anhydride reagent at time t=0. Under these circumstances the reaction becomes pseudo first-order, since the reaction rate is dependent upon the concentration of hydroxyl groups only, thus:

$$\frac{d[OH]}{dt} = -k'[OH] \qquad (2)$$

Where k' is the rate constant of the pseudo first-order reaction. An expression of this type can be rearranged and integrated [4,5,6] to give:

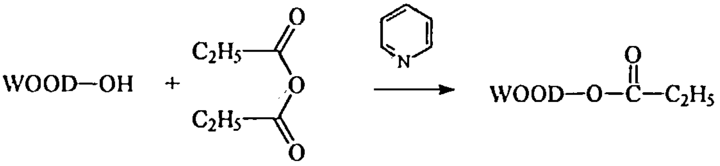

FIGURE 1. Reaction scheme.

$$\ln \frac{[OH]_t}{[OH]_o} = - k't \qquad (3)$$

Thus by plotting the natural logarithm of the concentration of hydroxyl groups substituted at time t , divided by the concentration at time=zero, against time in seconds a straight line is obtained with a gradient equal to the rate constant.

The activation energy of the reaction can be determined by measuring the rate constant at a series of temperatures. The Arrhenius expression defines the relationship between the rate constant and absolute temperature as:

$$k = \exp(-E_a/RT) \qquad (4)$$

Where E_a is the activation energy, T the absolute temperature, and R the gas constant. Thus a plot of the natural logarithm of the gas constant against the reciprocal of the absolute temperature, will give a straight line of slope $-(E_a/R)$.

Banks and West[7,8] investigated the kinetics of wood swelling with a variety of solvents, from which a series of activation energies for the swelling process were obtained. Recently, Mantanis et. al.[9-11] have further refined this work and obtained activation energies for a variety of swelling agents and wood species. In the pioneering work of West, it was assumed that the mechanism of swelling could be described by a bimolecular collision process of solvent molecules with wood reactive sites. By further assuming first-order kinetics during the initial part of the swelling process, a method was developed whereby activation energies could be determined from initial rates of reaction. The initial rate is proportional to the rate constant in a first order reaction, and in the classical Arrhenius plot the gradient and hence activation energy is determined by subtracting the natural logarithm of two rate terms. This is equivalent to dividing one rate term by the other, and hence the use of initial rates or rate constants is equally valid. Such an approach has been shown to yield very good Arrhenius plots, and it has become possible to determine activation energies for swelling processes for the first time as a result.

As part of a major effort to investigate the kinetic processes of wood modification reactions we decided to compare the method of initial rates with a conventional chemical kinetics method, in order to determine whether the two methods gave comparable results. Furthermore we also wished to determine whether the assumption that first order kinetics dominated the initial reaction process was valid. We chose the reaction of propionic anhydride with Corsican pine wood blocks swollen with pyridine as an experimental system, since preliminary studies had proven this to be a particularly suitable reaction system for studying the range of behaviour anticipated.

RESULTS AND DISCUSSION

Figure 2 shows a representative kinetic profile plot for the reaction of Corsican pine (*Pinus nigra*) blocks with propionic anhydride in pyridine at 90°C. The units of the y axis are given as the number of hydroxyl groups substituted per gm. of wood in mMoles per gram. This is equivalent to the number of moles of propionate groups substituted, and calculated by dividing the weight gain per gram of wood by the molecular weight of the substituting group (57.08 for the C_2H_5CO- group). This can be converted to a weight percent gain (WPG) by multiplying this value (in moles per gram) by a factor of 5.708×10^3. It can be seen that the profile exhibits asymptotic behaviour, tending towards a maximum value of ca. 5 mMoles per gram (a WPG of

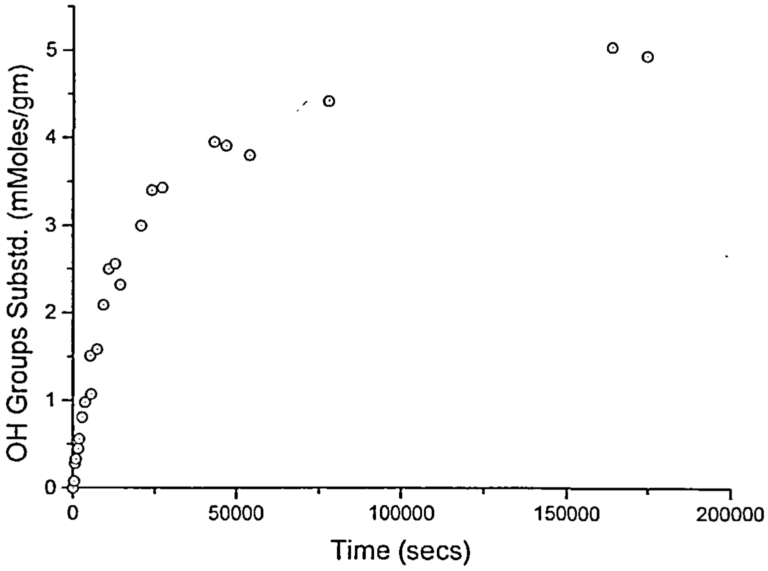

FIGURE 2. Kinetic profile of reaction of propionic anhydride with Corsican Pine at 90°C.

approximately 28.5%), where it is assumed that all available hydroxyl sites have reacted, after a total reaction time of approximately 48 hours. The initial rate of reaction is very rapid with 50% of total available sites substituted after 4 hours. A progressive slowing in reaction occurs thereafter. Figure 3 illustrates the same data but with the y axis expressed in terms of the dimensionless quantity $[OH]_t/[OH]_0$, where $[OH]_t$ is the concentration of OH groups per gm. remaining unreacted at time t and $[OH]_0$ the concentration of OH groups at zero time. A value for $[OH]_0$ of 14.9 mMoles of hydroxyl groups per gram of wood was used to calculate this figure. This value is an estimate of the concentration of hydroxyl groups in the wood calculated using the composition of Scots pine (*Pinus sylvestris*) as a model for Corsican pine [12] (see table 1).

The number of moles of hydroxyl groups per gram was then calculated from:

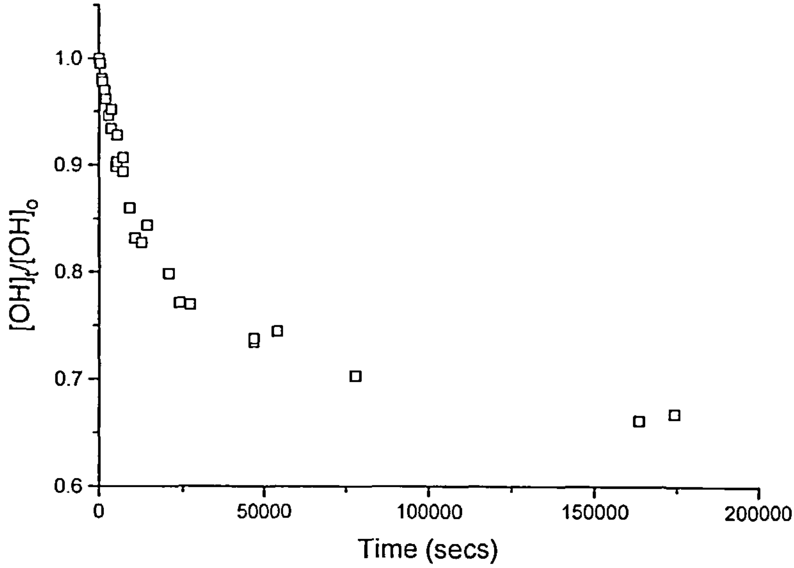

FIGURE 3. Kinetic profile of data points of figure 2, but with y-axis expressed in units of conc. unsubstituted hyroxyl groups at time t divided by conc. unsubstd. OH groups at t=0.

$$(0.26x1)/180+(0.52x3)/162+(0.14x3)/162+(0.08x2)/132 = 0.0149$$

Although this figure is an estimate and undoubtedly has an uncertainty associated with it, the error is of little significance at low substitution. The mole fraction of OH groups reacted is calculated from 1-($[OH_t/[OH]_0$), and multiplying this figure by 100 gives the percentage of OH groups reacted. It can be seen that the %OH groups reacted reaches a maximum of ca 35% at 90°C. This value is constant for propionic anhydride and does not depend upon temperature (although 120°C is an exception for reasons to be discussed later). The crystalline content of cellulose in whole wood has been estimated at around 65%[12], which suggests that a total of 8.6 mMoles of OH groups per gm. of wood (or 58% of total OH content) should be available for substitution, assuming that reactive sites are associated with amorphous sites in cellulose, hemicelluloses, and lignin. This estimate does not take

TABLE 1

Composition of *Pinus Sylvestris*.

Component	% Composition	OH Groups Per Unit[13]	Mol. Wt. Of Units
Lignin	26	$1/C_9$	180
Cellulose	52	$3/C_6$	162
Hexosan	14	$3/C_6$	162
Pentosan	8	$2/C_5$	132

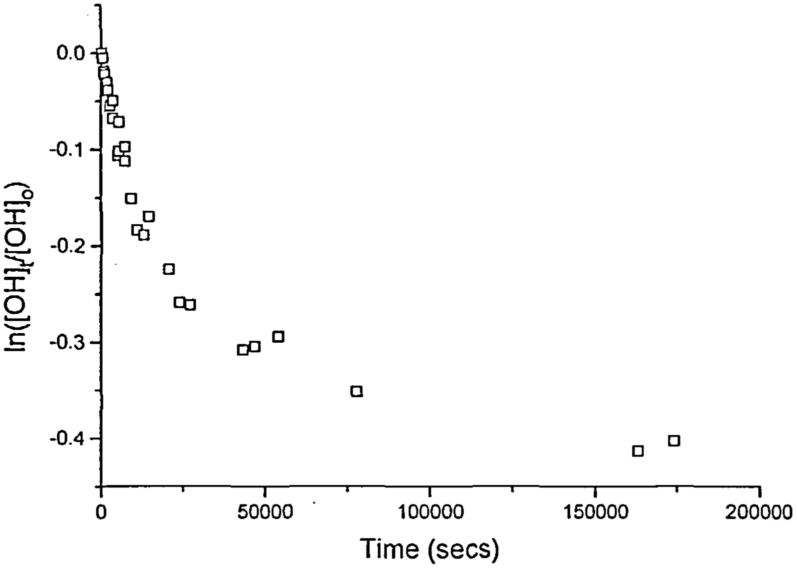

FIGURE 4. Plot of natural logarithm of $[OH]_t/[OH]_o$ against time for extended reaction periods. (90°C).

TABLE 2

Comparison of Rate Constant and Initial Rate Data

Temp. (K)	k' ($\times 10^{-5}$ s^{-1})	R_O ($\times 10^{-5}$ s^{-1})
393	-	16.06
383	7.20	11.89
373	2.48	5.01
363	1.98	2.76
353	1.65	2.45
343	1.07	1.77
333	1.06	1.42
323	0.79	0.89

account of OH sites that are sterically hindered, and this value will depend upon the bulk of the substituting group. We are currently studying the effect of reagent bulk, and results will be reported when the work is complete.

Figure 4 illustrates the relationship between the natural logarithm of the ratio $[OH]_t/[OH]_O$ and time. There is obviously no linear correlation here, but if the results are plotted up to a time of 5000 seconds as in figure 5, a very good linear correlation is obtained showing that the initial stages of the reaction do display first-order kinetics. Beyond a value of $[OH]_t/[OH]_O$ of 0.9 (or 10% of OH content substituted) this linear correlation is lost. If we attribute sites exhibiting first-order kinetics to surface hydroxyl's, this allows us to estimate that 10% of the wood hydroxyl content is associated with surface regions in samples of these dimensions. We are able to obtain a rate constant for this first-order region which gives us a value of 1.98×10^{-5} s^{-1}. By plotting data for different temperatures we have obtained the corresponding rate constants, and the data for this is shown in table 2. In addition to the rate constants (k'), we have also included data for the initial rates of reaction (R_O) obtained by curve fitting to the experimental points of figure 3, and equivalent plots at other temperatures then calculating the rate at time=0.

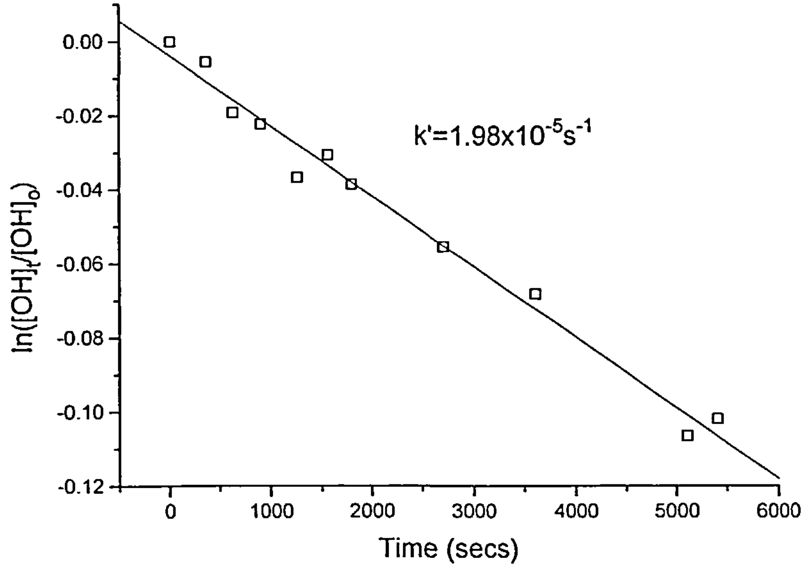

FIGURE 5. Plot of data of figure 4, but showing first order kinetics region.

The anomalous results obtained at 120°C (393 K) and 110°C (383 K) we attribute to damage occurring to the wood matrix, which becomes readily apparent to the eye after extended reaction times at 120°C. This clearly has serious implications when such wood modification reactions are undertaken, and we would recommend that reaction temperatures do not exceed 100°C in order to minimise sample degradation, at least when pyridine is used as a swelling agent with anhydride modifications.

Figure 6 shows the Arrhenius plots obtained from the rate constant and initial rate data shown in table 2. For the rate constant data the gradient of the straight line yields an activation energy for the pyridine catalysed reaction of 23.84 ± 0.27 kJ mol^{-1}, with an R^2 coefficient of 0.9644; but using the initial rate data, the activation energy is calculated to be 31.30 ± 0.36 KJ mol^{-1} with an R^2 coefficient of 0.9769. This is a significant difference. We do not attribute this difference to errors in measurement of initial rates or rate constants. Rather, the explanation for this anomaly is given in figure 7, which

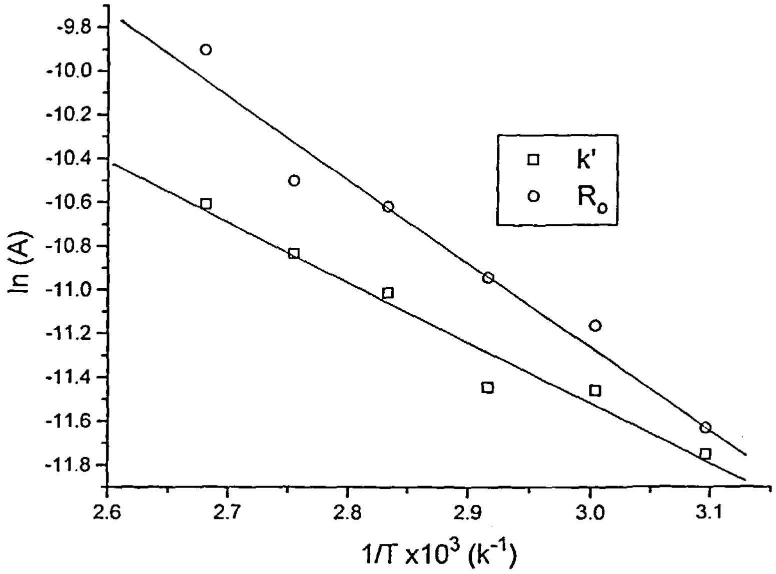

FIGURE 6. Arrhenius plot comparing initial rate (R_0) and rate constant (k') data.

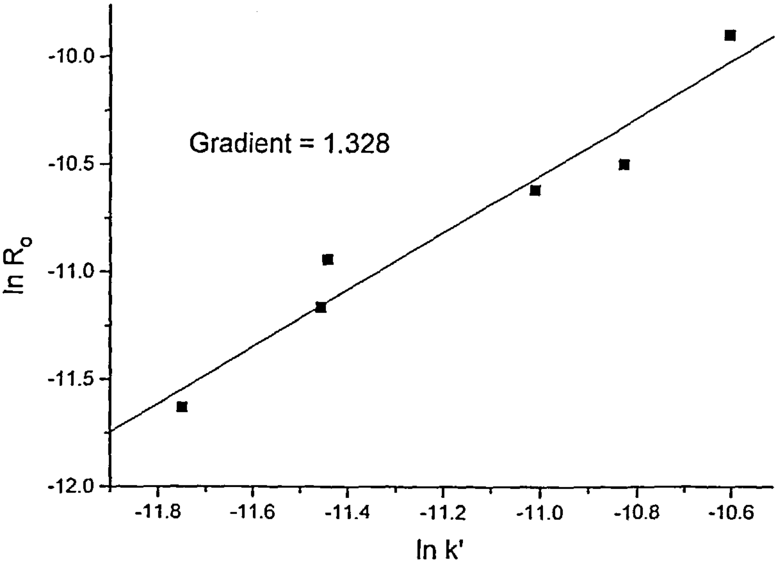

FIGURE 7. Relationship between natural logarithm of initial rate and natural logarithm of rate constant data.

illustrates the relationship between $\ln(R_0)$ and $\ln(k')$. Allowing for experimental error, a reasonable linear relationship is obtained between the two sets of data, which is in accordance with the reaction process exhibiting first order kinetics. From equation 2 the initial rate is equal to the rate constant multiplied by the concentration of hydroxyl groups at zero time. If we assume that the value of $[OH_0]$ is invariant with temperature, then a linear correlation between $\ln(R_0)$ and $\ln(k')$ is obtained with a gradient of 1.00. Instead we observe a gradient of 1.33, accounting for the difference in activation energies which have a ratio of 1.32. This difference in the E_a values we attribute to a variation in the number of available reactive hydroxyl groups at zero time. It is known that wood swollen with pyridine exhibits temperature dependent swelling, which would further complicate the observed kinetics. We therefore urge caution when quoting activation energies in chemical modification studies, particularly when a swelling solvent is used. We are currently extending our work to include the effects of non-participatory solvents such as toluene, as well as reactions with neat anhydride reagents.

EXPERIMENTAL

Blocks of. Corsican Pine sapwood (2cm x 2cm x 0.5cm: radial, tangential, longitudinal), were extracted with a mixture of toluene/acetone/methanol (4:1:1 by volume) for 6 hours, then oven dried overnight at 105°C. For a given reaction five labelled (2B pencil) replicate blocks were allowed to cool to ambient temperature in a dessicator over silica gel, then weighed rapidly on a four figure balance. The blocks were then added to a reaction flask together with 100ml of dry (over KOH) pyridine. The flask was evacuated using a diaphragm pump and the blocks subjected to five vacuum cycles over a period of one hour in order to ensure full impregnation with pyridine. The flask was then placed in an oil bath set to the required temperature (accurate to ± 0.25°C and allowed to equilibrate for one hour. To the flask was then added one molar equivalent of propionic anhydride (based on OD weight of blocks) dissolved in pyridine to make a total volume of 25 ml (pre-heated to the required temperature). A condenser was fitted to the flask and the blocks left to react for the required time. The reaction was quenched by removing the flask from the oil bath decanting off the hot reagent solution and adding the blocks to acetone. The time of addition of the blocks to the acetone was noted as the time of termination of the reaction. Once the blocks had cooled to ambient temperature, they were extracted in a Soxhlet apparatus as before then dried in an oven overnight prior to re-weighing.

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