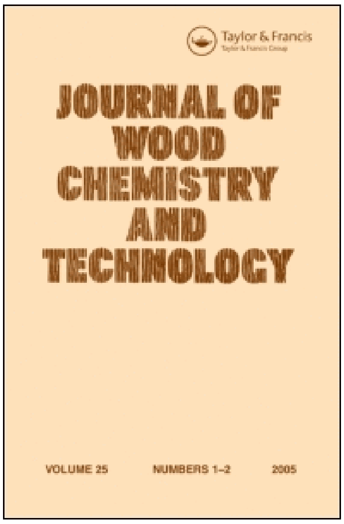

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THE CHEMICAL MODIFICATION OF SCOTS PINE WITH SUCCINIC ANHYDRIDE OR OCTENYL SUCCINIC ANHYDRIDE.
II. REACTION KINETICS

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ABSTRACT

The kinetics of the pyridine-catalyzed reaction of succinic anhydride (SA) and octenyl succinic anhydride (OSA) with Scots pine (*Pinus sylvestris*) have been investigated, and activation energies determined. The activation energies for surface reactions between wood and SA or OSA were determined as 79.5 (±13.0) and 29.6 (± 4.6) kJ/mol respectively. The low value of the latter activation energy, suggests that hydrogen bond breaking is a rate determining step with the reaction of OSA with wood. With SA the activation energy is of a similar magnitude to literature values for anhydride-alcohol reactions. The kinetics of reaction over extended time was analysed to see if diffusion dominated the process, complex profiles were observed which were not amenable to simple analysis.

INTRODUCTION

Chemical modification of wood using acetic anhydride is a well established technique for imparting dimensional stability and enhancing durability.[1,2] In addition, modification with cyclic anhydride reagents provides a material with covalently attached carboxylic acid functional groups, upon which further reactions can be performed.[3] Although many publications have appeared related to anhydride modification, the kinetics of such reactions remains a poorly studied area. Indeed, the investigation of such reactions with other heterogeneous substrates has received little attention.

Due to the commercial importance of cellulose acetate, the kinetics of acetylation of cotton linters with acetic acid has been well studied.[4] The rate curves of such reactions were found to be the sum of two reaction processes, one fast and one slow. These two processes were assigned to reaction with surface and bulk hydroxyl groups respectively, with the former displaying the kinetic processes of homogeneous acetylation. With the bulk OH groups, it was considered that the reaction was limited by the time taken for the reagent to penetrate to the reactive OH groups, and that diffusion into the cell wall was the rate limiting step. By determining the rate of the diffusion limited reaction at different temperatures, the activation energy (E_a) for the process was estimated to be 11.8 kJ/mol. The surface reactions were found to obey first-order kinetics, since the acetylating reagent was present in large excess. Further analysis showed that two reactions were occurring simultaneously, acetylation and deacetylation with associated activation energies of 49.7 kJ/mol and 59.8 kJ/mol. The kinetics of acetylation of cotton and jute fibres with a variety of acetylating systems was studied, and the results interpreted using diffusion models.[5] Two different mechanisms were identified with the two fibre types. Activation energies were determined as 71 kJ/mol for cotton and 54 kJ/mol for jute.

The kinetics of reaction of propionic anhydride with Corsican pine (*Pinus nigra*) with pyridine as catalyst, was found to obey pseudo first-order kinetics during the initial part of the reaction.[6] By determining reaction rates at different temperatures, the activation energy was calculated as 31 kJ/mol using rate constants. In addition, the method of initial rates ,developed by West,[7] was used to give a value of 24 kJ/mol. A study of the acetylation of Southern yellow pine, Deal, Sitka spruce and Larch has shown that the substrate may affect the activation energy of the reaction.[8] Unfortunately, the use of only three data points in the Arrhenius plots used to obtain the activation energies casts some doubt as to the accuracy of this observation. Acetylation of Corsican pine using pyridine as solvent/catalyst and with neat anhydride reagent has shown that the reaction kinetics are diffusion controlled, with no evidence of first order kinetics during the initial stages of the reaction.[9] Activation energies of 41.6 kJ/mol (pyridine catalyzed) and 50.9 kJ/mol (uncatalyzed) were obtained using the method of initial rates. Additionally, activation energies of diffusion were determined as 20.5 kJ/mol (catalyzed) and 34.2 kJ/mol (uncatalyzed).

As part of an extensive investigation of the kinetics and mechanism of the anhydride modification of wood, a study has been performed upon the reaction of two cyclic anhydrides with Scots pine (*Pinus sylvestris*), using pyridine as solvent/catalyst. The two anhydrides chosen were succinic anhydride (SA) (Fig. 1a), and 2-Octen-1-yl succinic anhydride (OSA) (Fig. 1b).

RESULTS AND DISCUSSION

Surface reactions

On a molecular scale, the reaction of anhydride reagents with wood may be viewed as occurring with surface or bulk OH sites. Reaction with

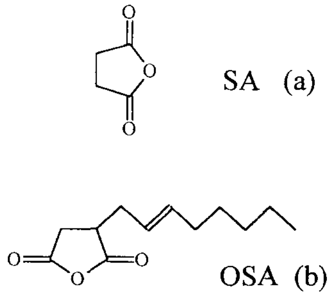

FIGURE 1. Structures of the molecules referred to in the text, succinic anhydride (SA) (a), 2-octen-1-yl succinic anhydride (OSA) (b).

surface OH sites can be considered to be an homogeneous kinetic process, which will obey first-order rate laws.[6] If first order kinetics dominates the reaction process then the following relationship is obeyed:

$$\mathbf{d[OH]/dt = -k[OH]} \qquad \mathbf{(1)}$$

Where **[OH]** is the concentration of hydroxyl groups, **k** is the rate constant of the reaction and **t** is time. Such an expression may be rearranged and integrated to give:

$$\mathbf{\ln([OH]_t/[OH]_0) = -kt} \qquad \mathbf{(2)}$$

Where $\mathbf{[OH]_t}$ and $\mathbf{[OH]_0}$ are the concentration of unsubstituted OH groups at time = t, and time = 0 seconds respectively. The value $[OH]_0$ was calculated as 14.9 mmoles/gm of oven dry wood.[6] Thus by plotting the natural logarithm of $[OH]_t/[OH]_0$ versus time, a straight line relationship is obtained if first-order kinetics is obeyed. The slope of the straight line is equal to the rate constant of the reaction. By determining the magnitude of k at different temperatures, the activation energy can be found by using the well known Arrhenius expression:

$$\mathbf{k = A\exp(-E_a/RT)} \tag{3}$$

Where **E_a** is the activation energy of the reaction, **R** the universal gas constant, **T** the absolute temperature, and **A** the pre-exponential (collision) factor. Attempts to analyse the reaction profiles in terms of first-order kinetics were not successful, with no straight line relationship being obeyed for SA nor OSA. In order to determine the activation energies for the surface reaction, it was therefore necessary to rely upon the method of initial rates. The method relies upon determining the rate of reaction at time=0 seconds (**R_0**) , which is:

$$\mathbf{R_0 = -k[OH]_0} \tag{4}$$

Thus, providing that the quantity $[OH]_0$ is temperature independent, then the activation energy of the reaction can be determined by substituting R_0 for k in the Arrhenius expression. It was found that in the case of the reaction of propionic anhydride with Corsican pine using pyridine as catalyst, that different values for the activation energy were obtained using the two methods. Hence although the initial rates methods is useful, the values of E_a that are obtained from it may be subject to some error. However it still provides a means for comparison between various reagents.

Figure two shows a typical reaction profile for reaction of OSA at 100°C, with an appropriate curve fit. The initial rates method is a means whereby the activation energy of reaction at time zero may be determined, that is by definition, reaction at surface sites only. Since the method relied upon here uses curve fitting to a number of data points, it is necessary to

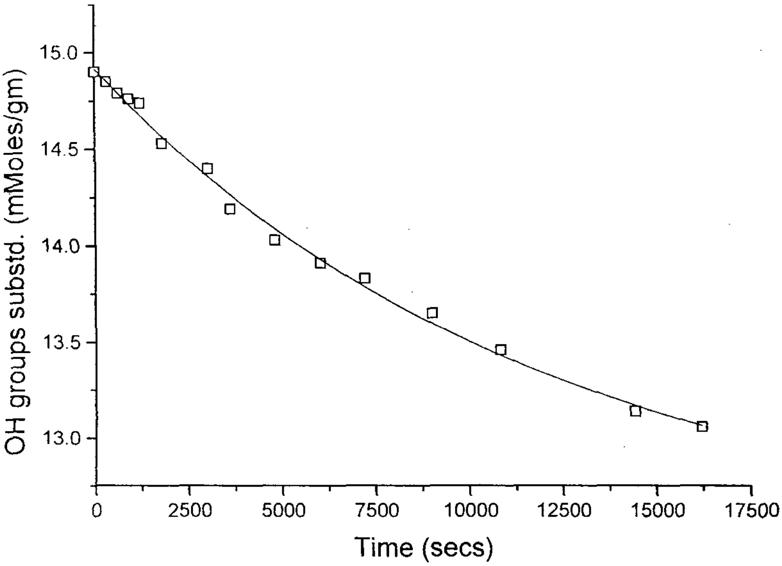

FIGURE 2. Typical curve fit (exponential decay) to data points for reaction of OSA with Scots pine at 100°C for initial part of reaction.

use data from the early stages of the reaction only, since the fit will be distorted as (or if) the reaction kinetics becomes diffusion dominated. The fitting function chosen for this was an exponential decay function. Although this choice was arbitrary, it was found empirically that this gave the best fits to the data points of the initial reaction process, however, no conclusions are drawn from this. A suitable fitting function to describe the whole reaction profile is under development. An important factor for selecting the best fit (apart from fitting the data points) was that the curve must pass through 14.9 mMoles/gm at zero time, otherwise the initial rate is not determined.

From the parameters obtained from the fit, it is then possible to obtain the gradient at time zero. This has been done for a number of

TABLE 1

Activation Energies (in kJ/mol) for Reaction of Acetic Anhydride with Alcohols in Homogeneous Systems

E_a	*Alcohol*	*Solvent*	*Ref.*
51.9	Methanol	CCl_4	11
57.7	Ethanol	CCl_4	11
78.7	Ethanol	Ethanol	12
51.9	Ethanol	Hexane	12
66.1	Ethanol	CCl_4	12
72.3	Ethanol	Ethanol	13
58.1	Ethanol	CCl_4	13
47.2	Ethanol	Heptane	13

temperatures ranging from 120°C to 60°C in 10°C increments, for both SA and OSA. From these gradients the Arrhenius plots shown in Figure three were obtained. From the linear fits of these, the activation energies for the initial reaction were calculated as:

79.5 (± 13.0) kJ/mol for SA ($R^2 = 0.883$)
29.6 (± 4.6) kJ/mol for OSA ($R^2 = 0.894$)

A value of 57.5 kJ/mol for the reaction of phthalic anhydride with glycerol in the formation of alkyd resins has been quoted.[14] From comparison of the above values with those of Table 1, it can be seen that the E_a obtained for reaction of SA is in reasonable agreement with what might be expected for the chemical activation energy of the reaction of an anhydride with an alcoholic OH group, but that for OSA (and indeed propionic anhydride) are over 20 kJ/mol lower than anticipated. However, these latter values are close to the value of the bond strength of a hydrogen bond in wood, which has been estimated as *ca.* 25 kJ/mol.[10] This result suggests that with larger reagents, hydrogen bond breaking is the rate determining step in the reaction mechanism. This may be rationalised by consideration of the space required by a reagent in which it has to adopt a specific configuration with respect to the OH group in order to react, and that with larger reagents a greater volume is required, necessitating a change in the local cell wall polymer structure. This configurational change requires hydrogen bond breaking which is slow compared with the rate of reaction of the anhydride. This H-bond breaking has been considered by West with regard to reaction of isocyanates with wood,[7] although this appears to be the first time direct evidence has been obtained for this. It must be stressed that such a mechanism remains conjectural until work on other anhydrides (currently underway) is complete.

Bulk reactions

The determination of initial rates (and from these, activation energies) gives values related to surface reaction processes only. By definition, any reaction at time zero will be at the surface, since the reagent has not penetrated into the bulk of the material. As reaction proceeds, the diffusion of reagent becomes dominant. Whether diffusion processes are observed depends upon the relative rates of reaction and diffusion. Thus if diffusion is slow compared with reaction, then the former will represent a bottleneck of the process, and will be observed in the kinetic determination. In order to test whether diffusion processes are a factor in the reaction kinetics, plots of substitution of OH groups vs. square root time were made. An example for the reactions of OSA, SA and AA with Scots pine at a temperature of 100°C is given in Figure 4. Both OSA and SA exhibit sigmoidal relationships in this plot, with an initial induction

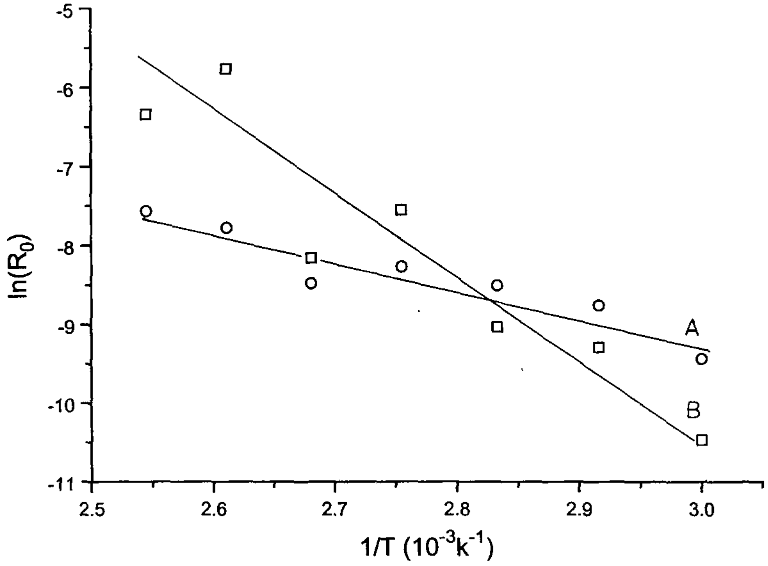

FIGURE 3. Arrhenius plot for reaction of octenyl succinic anhydride (squares, A) and octenyl succinic anhydride (circles, B) with Scots pine, from initial rate data.

period, and approximately linear middle region, AA exhibits a linear relationship during the initial part of the reaction. The sigmoidal relationship has been noted during studies of the acetylation of cotton and jute,[5] and with longer chain anhydrides.[15] The observation of such sigmoidal curves has been previously attributed to history-dependent diffusion.[5] A model to explain these observations is under development at present. The reaction profile observed with SA is unusual, in that a high level of OH substitution is achieved. The level of OH substitution seen with SA is greater than that with AA, even though the SA adduct occupies a greater volume than AA. It was noted that sample degradation occurred following modification with SA with reaction times in excess of one hour, as a consequence of this new reactive sites are made available in the

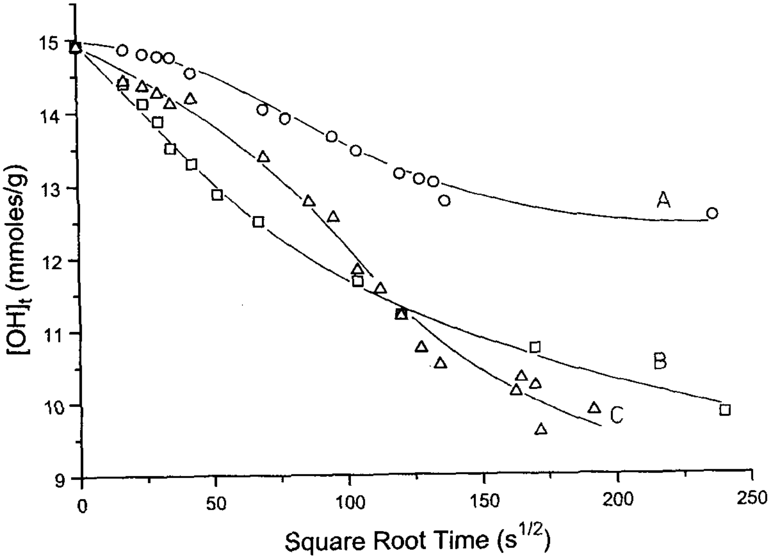

FIGURE 4. Diffusion plot for reaction of octenyl succinic (circles, A), acetic (squares, B), and succinic (triangles, C) anhydride with Scots pine at 100°C.

substrate. Such damage has been observed to lead to embrittlement of the wood samples.

CONCLUSIONS

The method of initial rates has been used to determine the activation energies of the reaction of succinic anhydride or octenyl succinic anhydride with Scots pine whole wood. The E_a's associated with surface reactions were found to be significantly different with the two reagents, with the larger of the two molecules exhibiting a lower activation energy (29.6 kJ/mol). With SA (E_a = 79.5 kJ/mol), the activation energy is close to what would be expected for a chemical process. It is suggested that the rate determining step in the reaction of OSA with wood is the breaking of hydrogen bonds within the polymeric network. It is possible that larger reagents exhibit this H-bond breaking as a rate determining step in the kinetic process. Further work is required to verify this tentative conclusion. Over extended reaction periods, analysis of the profiles to determine whether the reaction kinetics becomes diffusion dominated, has indicated complex behaviour for which a model is being developed. Evidence of sample damage occurring during modification of wood with SA has been observed.

EXPERIMENTAL

Scots pine (*Pinus sylvestris*) sapwood blocks (20mm x 20mm x 5mm; radial x tangential x longitudinal) were cut with the grain parallel to the tangential face. Samples were Soxhlet extracted using a solvent system of toluene: acetone: methanol (4:1:1, by volume) for six hours, then oven dried at 105°C overnight. The blocks were removed from the oven and placed in a vacuum dessicator over silica gel in order to cool to ambient temperature before weighing on a four-figure balance. Samples were modified using pyridine as catalyst, with an equimolar solution of the anhydride based upon an estimate of the OH concentration in the wood. Calculation of the OH concentration was performed according to the method reported previously.[6] Wood samples were vacuum impregnated with pyridine before addition to a round bottom flask containing 100 mL of pyridine, set in an oil bath at the desired temperature. The blocks were left to equilibrate at this temperature for a period of one hour, before addition of a per-heated solution of the anhydride in pyridine (25 mL). The reaction was terminated by decanting off the reagent solution, and then adding the samples to acetone at ambient temperature. Upon cooling, the samples were then transferred to a Soxhlet extractor and solvent extracted as previously, then dried in an oven at 105°C overnight. Samples were then removed, and allowed to cool in a dessicator before reweighing.

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