The Reaction of Crotonic Anhydride with Scots and Corsican Pine: Investigation of Kinetic Profiles and Determination of Activation Energies

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Abstract: The kinetics of the reaction of crotonic anhydride with Scots pine (*Pinus sylvestris*) and Corsican pine (*Pinus nigra*) using pyridine as catalyst/solvent was investigated and activation energies for the initial reaction determined. Activation energies were calculated from the Arrhenius equation using rate data obtained from time-course experiments repeated at several temperatures. In one method, reaction constants (k) were determined experimentally, while in the other method initial rates were extrapolated at time zero. With the rate constant method, activation energy values for Scots and Corsican pine were calculated as 39.0 (±5.8) and 30.3 (±6.8) kJ mol^{-1}, respectively. The method of initial rate was also used to determine activation energy. Activation energies of 41.3 (±7.0) and 26.9 (±4.0) kJ mol^{-1} were obtained for Scots and Corsican pine, respectively. There was no significant difference between the activation energies determined by the two methods. The initial reaction was observed to follow pseudo first-order-kinetics. A difference of *ca.* 10 kJ mol^{-1} between the activation energies was found between the two wood species. The reason for this difference is not known. This information is of fundamental importance when considering such issues as mechanisms of reaction, or designing efficient large scale processes.

Key Words: Activation energies, rate constant, initial rate, chemical modification

Sarıçam ve Karaçam ile Krotonik Anhidrit Reaksiyonu: Kinetik Profillerinin İncelenmesi ve Aktivasyon Enerjilerinin Belirlenmesi

Özet: Krotonik anhidrit ile Sarıçam ve Karaçamın pridin katalizatör eşliğindeki reaksiyon kinetiği incelenmiş ve başlangıç reaksiyonları için aktivasyon enerjileri tespit edilmiştir. Aktivasyon enerjileri bir çok farklı sıcaklık derecelerinin kullanılarak zaman aşaması deneylerinden elde edilen oran verilerinin Arrhenius eşitliği kullanılarak hesaplanmıştır. İlk metotta reaksiyon sabitesi (k) deneysel olarak belirlenmiş, diğer metotta ise başlangıç oranı sıfır zamanı için hesaplanmıştır. Sarıçam ve Karaçamın oran sabitesi metodu ile aktivasyon enerjisi değerleri sırasıyla 39,0 (±5.8) and 30.3 (±6.8) kJ mol^{-1} olarak hesaplanmıştır. Aktivasyon enerjilerinin belirlenmesinde başlangıç oran metoduda kullanılmıştır. Sarıçam ve Karaçam örnekleri için sırasıyla 41.3 (±7.0) ve 26.9 (±4.0) kJ mol^{-1} değerleri elde edilmiştir. Her iki yöntemle belirlenen aktivasyon enerjisi değerleri arasında belirgin bir fark bulunamamıştır. Başlangıç reaksiyonunda pseudo first order kinetik gözlemlenmiştir. İki odun türü arasında yaklaşık 10 kJ mol^{-1}'lük aktivasyon enerjisi farklılığı bulunmuştur. Bu farkın sebebi bilinememiştir. Bu bilgiler reaksiyon mekanizmasının anlaşılması veya büyük ölçekli üretimlerin etkin olarak dizayn edilmesi ve benzeri konuların değerlendirilmesinde temel önem taşımaktadır.

Anahtar Sözcükler: Aktivasyon enerjisi, oran sabitesi, başlangıç oranı, kimyasal modifikasyon

Introduction

The chemical modification of wood using anhydride reagents is a long established area of research (Stamm and Tarkow, 1947). Although the subject of many research papers, reaction kinetics remains a poorly studied area. Wood is a far from ideal substrate on which to perform such studies, due to its complex heterogeneous physical and chemical composition. It is expected that this complexity will be reflected in the nature of the reaction profiles observed. Nonetheless, it has proved possible to determine activation energies for reactions of acetic (Hill et al., 1998) and propionic (Hill and Jones, 1996) anhydrides with Corsican pine, succinic, and octenyl succinic (Hill and Mallon, 1988) anhydrides with Scots pine by using the method of initial rates (West, 1988), and additionally using rate constants in the case of propionic anhydride. The activation energies in these studies are due to processes which dominate during the

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initial stages of the reaction, and as such have been assumed to be related to the surface sites of the substrate. Additionally, with both acetic and octenyl succinic anhydrides, it has proved possible to determine activation energies for the diffusion dominated part of the reaction profile. All of these reactions were performed using pyridine as solvent/catalyst. This work has now been further extended to crotonic anhydride (Figure 1), and additionally to determine the effect of substrate upon kinetic profiles and activation energies.

Materials and Methods

Samples of Scots or Corsican pine sapwood blocks 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were cut from sapwood and extracted in a Soxhlet apparatus for 8 h using a solvent system of toluene:acetone:methanol (4:1:1, by volume). Extractive free samples were dried in an oven overnight at 105 °C, allowed to cool in a desiccator over silica gel and then weighed on a four figure balance. For the modification reaction, five replicates were vacuum impregnated with pyridine, transferred to a round bottom flask and immersed in pyridine. The flask was transferred to an oil bath and heated at the required temperature for 1 h. Excess pyridine was then decanted off, and a pre-heated solution containing an equimolar amount of crotonic anhydride in pyridine (total volume 25 ml) added. A condenser was fitted to the flask and the reaction was allowed to proceed for a pre-determined time. The reaction was terminated by decanting off the hot solution and adding acetone. The flask and contents were left for 30 min, and then the modified samples were transferred to a Soxhlet, extracted as mentioned previously, oven dried and re-weighed.

Results and Discussion

Kinetic Profiles

A typical reaction profile for the modification of Scots (squares) and Corsican (circles) pine with crotonic anhyride at 120 °C is shown in Figure 2. It can be seen from this plot that the reaction profiles are very similar for the two substrates in this study, although the initial reaction proceeds more rapidly with Scots pine. It is of interest to note that above a weight percent gain (wpg) of *ca.* 30%, that there is some difference in behaviour; this was also observed at other temperatures. In both cases, the reaction profile flattens off at 30% wpg, but then begins to rise again with an ultimate weight percent gain of 42-43% being achieved after 72 h.

These are very high levels of modification, not normally observed with linear chain anhydrides under these conditions. The degree of substitution of the OH groups was calculated according to methods given in a previous paper (Hill et al., 1998). If crotonic anhydride obeyed this relationship, then an ultimate degree of substitution of *ca.* 4.5 mmol of OH groups per gram of wood would be predicted. The molecular weight of the crotonyl adduct is 69.09, thus the expected maximum level of substitution in terms of wpg is calculated to be *ca.* 31.5%. This value corresponds to where the initial part of the reaction levels off. This behaviour may therefore be attributed to additional reaction occurring with the substrate. This may possibly be due to sample damage, allowing access of the reagent to previously unreacted regions of the substrate, or to a reaction occurring at the double bond of the crotonyl group. The latter would be a slow process due to steric hindrance at the double bond. This behaviour is commonly observed with crotonic anhydride modification as exemplified in Figure 3 for the reaction of Corsican pine samples at several temperatures (100, 80 °C), where it can be seen that a slowing of the reaction rate occurs at essentially the same time, but at different levels of substitution. It should also be noted that the predicted substitution level of 4.5 mmol g^{-1} is exceeded in all cases.

By plotting the volume change against weight percent gain, it is possible to determine whether substrate degradation is occurring (Figure 4). Above a volume change of 15%, the swelling of the substrate due to
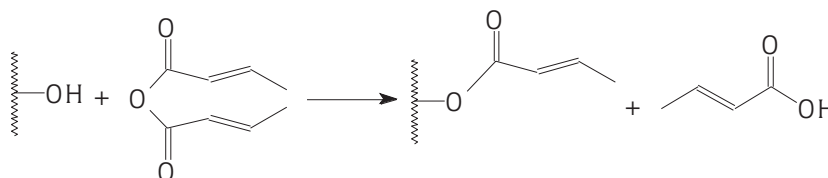
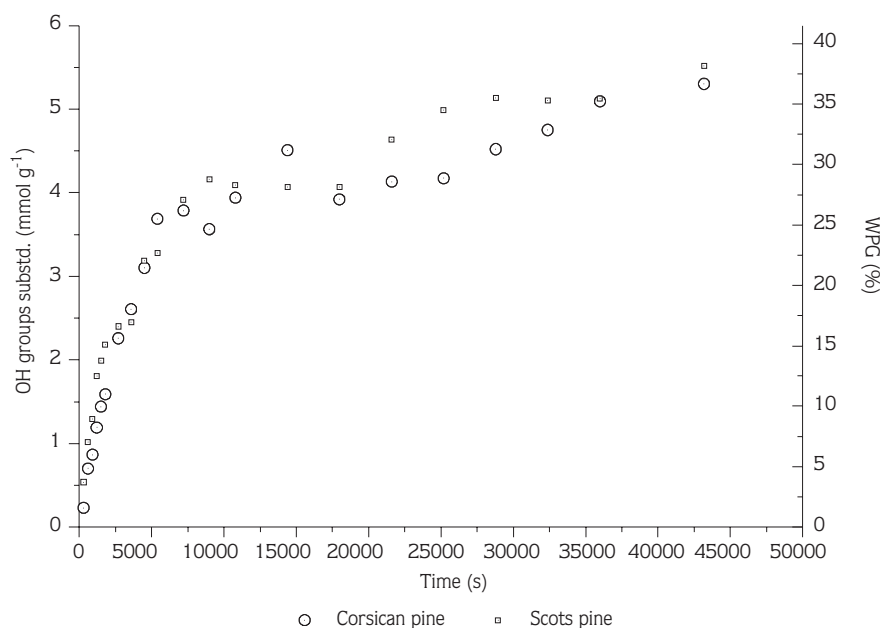Figure 1.   Reaction scheme for the reaction of crotonic anhydride with wood.

Figure 2.   Reaction profile for the reaction of crotonic anhydride with Scots (squares) and Corsican pine (circles) at 120 °C.
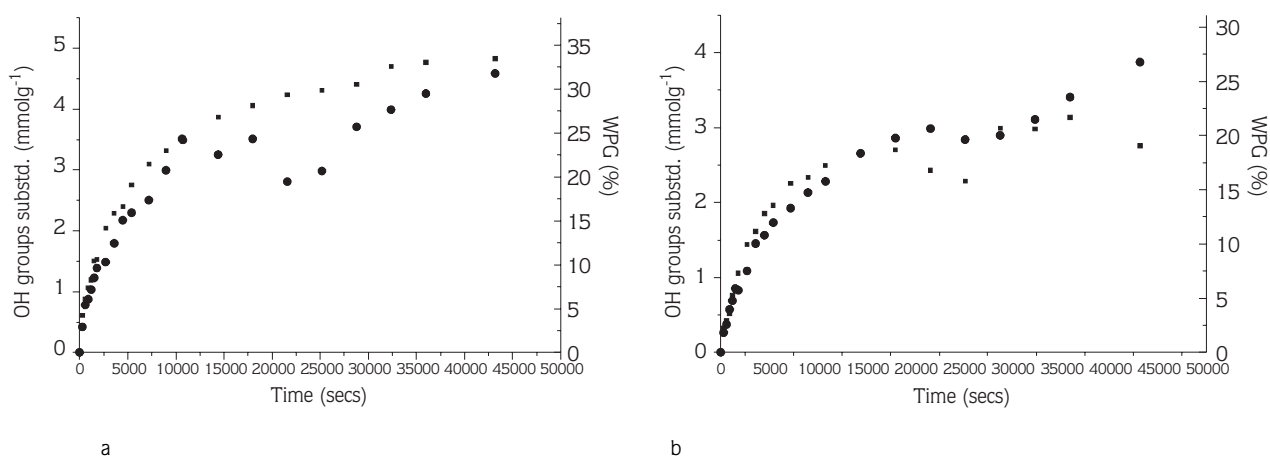

Figure 3.   Reaction profile for the reaction of crotonic anhydride with Scots (squares) and Corsican pine (circles) at 100 °C (a) and 80 °C (b).

modification increases at a greater rate than below this wpg value in a non-proportional manner. The value of 15% is equivalent to the maximum swelling of the substrate in water soak tests. This indicates that substrate degradation is indeed occurring above a threshold of 30% wpg, possibly explaining the anomalous results.

Below 120 °C, the same behaviour was observed with volume change being proportional to wpg up to a wpg of

30%, although the deviation from this line is less at lower temperatures. Although this explains the reason for the double curve at 120°C, the explanation at lower temperatures is not apparent. If degradation were a time dependent phenomenon, then deviations from proportionality in the volume change-wpg plot would occur at various wpg's, but this is not observed. However, it should be noted that a similar plot for the reaction of alkenyl succinic anhydride with Scots pine

exhibits linearity up to a wpg of 40% and a volumetric swelling of 25%, yet degradation is clearly visible to the naked eye at these levels of substitution (Mallon, 1999).

Activation Energies

The wood anhydride reaction can be represented as shown in Figure 1. The rate expression for such a chemical reaction scheme is as follows: $d[OH]/dt = -k[OH][anhyd]$, 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 the 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, $d[OH]/dt = -k'[OH]$, where k' is the rate constant of the pseudo-first-order reaction. An expression of this type can be rearranged and integrated to give $\ln [OH]_t/[OH]_0 = -k't$.

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 quantities $[OH]_t$ and $[OH]_0$ are the concentration of OH groups in the wood at time = t and time = 0 respectively, and are calculated from the estimate of 14.9 mmol g^{-1} of OH groups in untreated wood [calculation of these estimates values are shown in another publication (Callum and Jones, 1996)]. The number of moles of substituted OH groups is calculated by determining the weight gain per gram dried wood and dividing by the molecular weight of the crotonic adduct (69.09). This value is then subtracted from $[OH]_0$ to give $[OH]_t$. A typical plot for the reaction of crotonic anhydride with Scots pine at 120 °C is shown in Figure 5. By determining the rate constants at a series of temperatures it is then possible to evaluate the activation energy for the reaction by using the well known Arrhenius expression:

$$k = A \cdot exp\ (–Ea\ /\ RT)$$

where k is the rate constant, A the pre-exponential (collision) factor, Ea the activation energy, R the universal gas constant, and T the absolute temperature. By taking natural logarithms of both sides of the equation, a straight line relationship is obtained if the Arrhenius equation is obeyed, with gradient equal to $–Ea/R$. This is shown for both wood species in Figures 7 (Scots) and 8 (Corsican). From these plots, activation energies of 39.0 (+/- 5.8) ($R^2 = 0.9$), and 30.3 (+/- 6.8) kJ mol^{-1} ($R^2 = 0.8$) were obtained for Scots and Corsican pine, respectively. Although the Ea for Scots pine is larger, it is not possible to say how significant this difference is when considering measurement errors.
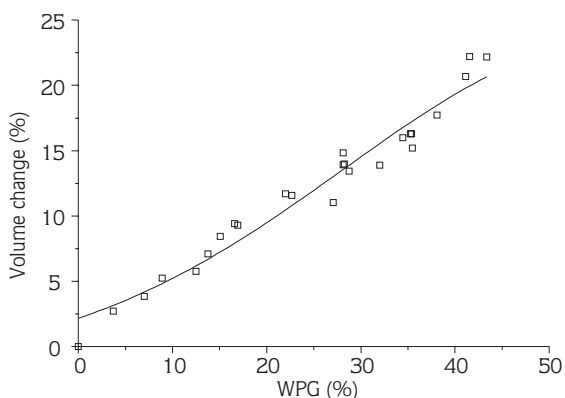

Figure 4.   Relationship between weight percent gain (WPG %) and percentage volume change for the reaction of crotonic anhydride with Scots pine at 120 ℃.
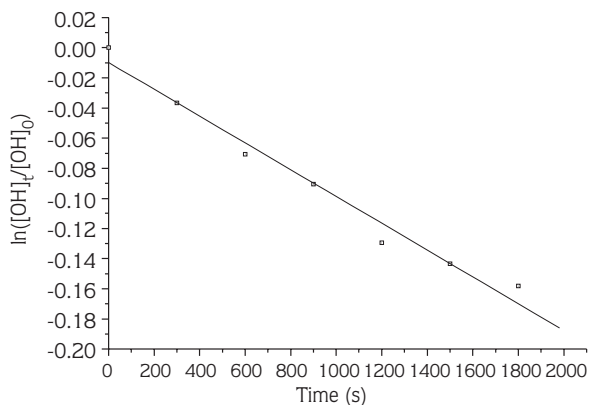

Figure 5.   First- order kinetics plot of crotonic anhydride at 120 ℃ (Scots pine) ($R^2 = 0.98$).

The method of initial rates was also used to determine the activation energies for the reaction. In order to use this method, it is necessary to determine the rate curve for the initial part of the reaction. An example is given for the reaction with Scots pine (Figure 6) at 120 °C; an exponential curve fit was used to determine the initial rate, the gradient at time zero being determined from the parameters of the fit to give the initial rate (R_0).

This data was then used to give the Arhenius plots shown in Figures 7 and 8. The linear fits give activation energies of 41.3 (+/-7.0) ($R^2 = 0.86$) and 26.9 (+/-4.0) kJ mol^{-1} ($R^2 = 0.9$) for Scots and Corsican pine, respectively. Using the two methods it is concluded that the activation energy for the reaction of crotonic anhydride with Corsican pine is of the order 30 kJ mol^{-1}, and with Scots pine *ca.* 40 kJ mol^{-1}.

It is not known whether this difference represents a true variation related to the wood species, or is artefactual due to ultrastructural differences (number of growth rings, thickness of early wood/late wood bands etc.). Work is ongoing to investigate this matter.

It is instructive at this point to compare these results with those previously determined with other anhydride reagents (Hill et al., 1998; Hill and Jones, 1996a; Hill and Mallon, 1999). The conditions used for the study of the kinetic profiles in this work differ from those in previous reports (Hill and Jones, 1996a; Hill et al., 1998), in that a higher concentration of reagent was used (3 molar compared with 0.6 molar). A higher concentration was necessary since it was found that the reaction of wood

with these reagents at low temperatures was slow, and the associated kinetic profile exhibited a high degree of scatter of data points, making analysis difficult. Although the concentration was higher, the solutions contained an equimolar quantity of reagent based upon estimates of the OH group concentration in the samples, as with previous studies (Hill and Jones, 1996a; Hill et al., 1998). It should be noted that although the higher concentration of reagents will lead to an increase in the reaction rate, the activation energies remain unaffected since these are determined by the effect of temperature on the rates. The data obtained from this set of experiments and from that reported in the literature with acetic (Hill et al., 1998), propionic (Hill and Jones, 1996a), succinic and octenyl succinic anhydrides (Hill and Mallon, 1999) is combined in Table 1.

The large difference in Ea measured using initial rates and rate constant methods with propionic anhydride (Hill and Jones, 1996) does not occur with crotonic anhydride in either wood species. All of the activation energies thus far determined fall within the region 30-40 kJ mol^{-1} with one exception, succinic anhydride (Hill and Mallon, 1999).

Several points arise from this comparison in Table 1. There is a general trend toward lower activation energies as the molecular weight of the reagent increases. With anhydrides larger than acetic anhydride, it has been postulated that the reaction requires the breaking of the cell wall polymer H-bonding network in order to create a sufficiently large void space in the cell wall to accommodate the reagent (West, 1988; Hill et al., 1998). If this is so, then it would be expected that the volume of
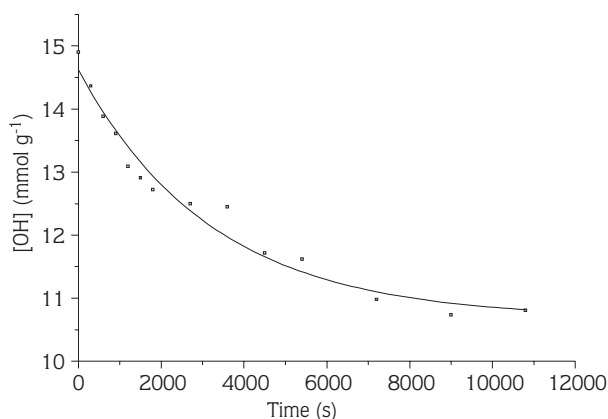

Figure 6. Exponential curve fit to initial reaction data for the reaction of crotonic anhydride with Scots pine at 120 °C.
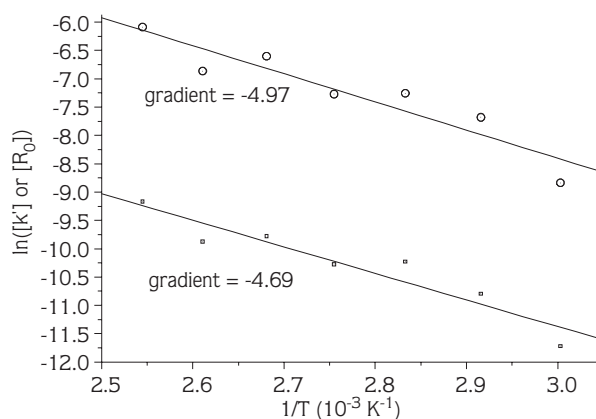

Figure 7. Arrhenius plot for the reaction of crotonic anhydride with Scots pine using rate constant (k') (square) ($R^2 = 0.90$) and initial rate (Ro) (circle) ($R^2 = 0.86$).
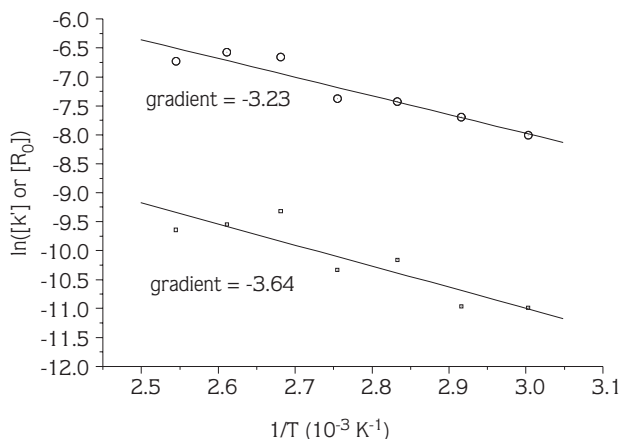
Figure 8.   Arrhenius plot for the reaction of crotonic anhydride with Corsican pine using rate constant (k') (square) (R^2 = 0.8) and initial rate (Ro) (circle) (R^2 = 0.9).

Table 1.   Experimentally determined activation energies for reaction of anhydride reagents with Scots or Corsican pine (a = Scots pine).

Anhydride	Ea (R0)	Ea (k)	Ref
Acetic	41.6 (+/-8.0)	n/a	Hill et al., 1998
Propionic	31.3 (+/-0.4)	23.8 (+/-0.3)	Hill and Jones, 1996
Crotonic	26.9 (+/-4.0)	30.3 (+/-6.8)	-
Crotonic[a]	41.3 (+/-7.0)	39.0 (+/-5.8)	-
Succinic[a]	79.5 (+/-13.0)	n/a	Hill and Mallon, 1999
Octenyl Succinic[a]	29.6 (+/-4.6)	n/a	Hill and Mallon, 1999

the reagent has an influence upon the activation energy. This has been investigated by plotting the relationship between molar volume of the reagent against activation energy determined by the initial rates method for Corsican pine (Figure 9).

It is observed that a curvilinear relationship is obtained for all of the anhydrides. The activation energy of anhydrides with Corsican pine decreases as the molar volume of the reagent increases. The reason for this relationship is not clear, although it is apparent that the reagent volume is an important factor in determining activation energy. It is difficult at present to draw any
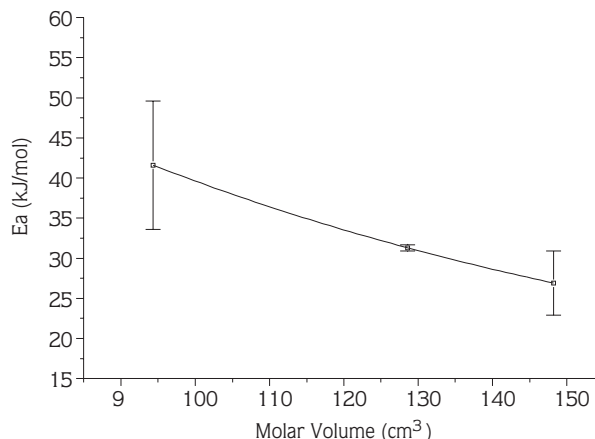

Figure 9   Relationship between activation energy and molar volume of reagent [a- acetic (Hill et al., 1998); b- propionic (Hill and Jones, 1996a); c- crotonic anhydride], for the reaction of Corsican pine, and using activation energies determined from initial rate data

definite conclusions regarding the significance of the activation energies for wood modification reactions.

Conclusions

The kinetic profile for the reaction of crotonic anhydride with Corsican and Scots pine exhibits different behaviour compared with those observed with other anhydrides. In addition, very high weight percent gains are obtained. A reaction with the double bond of the attached crotonyl group is implicated in this behaviour, although no evidence for such a reaction has been found spectroscopically. This additional reaction may in turn lead to degradation of the substrate allowing for new OH sites to become available for reaction. Further investigations are underway to determine the mechanism of this process. Determinations of activation energies of crotonylation by the methods of initial rates and rate constant have given comparable values, in contrast with earlier work on propionylation. A difference in activation energy has been found between Scots and Corsican pine, but the reason for this is not known.

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