THERMOGRAVIMETRIC INVESTIGATION OF THE PYROLYSIS OF PITCH MATERIALS. A COMPENSATION EFFECT AND VARIATION IN KINETIC PARAMETERS WITH HEATING RATE

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ABSTRACT

Thermogravimetric measurements of weight loss accompanying the pyrolysis of four pitches have been made over a range of linear heating rates. For three of the samples, the data at each heating rate could be described by an integral and a differential method of analysis, assuming a simple order function for $f(\alpha)$, with the result that the apparent activation energy increased with heating rate. The data for all four samples could also be satisfactorily described by the Ozawa or Friedman multiple heating rate methods, and these resulted in apparent activation energies (E_a) which increased with the value of β at which they were determined. It is suggested that this tendency for the apparent activation energy to increase, as the temperature is raised, is due to a change in the relative importance of the different reactions which lead to weight loss in this system. The apparent kinetic parameters all fall on a common compensation plot which is used to explain the relative magnitude of E_a values from Ozawa and Doyle methods of analysis. The higher values of E_a from Friedman than from Ozawa analyses are also explained.

INTRODUCTION

The pyrolysis of pitch materials in an inert atmosphere is an important step in the production of cokes which are used in the manufacture of graphite materials. During the manufacturing process, a pitch material is also used to bind the coke granules and this is subsequently carbonised. In such applications, the technique of non-isothermal thermogravimetry is a useful method of assessing the temperature range of pyrolysis, the temperature of maximum rate of volatilization and the subsequent yield of coke, all of which are important technological parameters in the manufacturing operation. However, from time to time attempts have been made to determine kinetic parameters from such measurements and to use these also to characterise the pitches.

In common with other studies in the field of solid state decompositions, it

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has been common practice to assume the rate expression to be of the form

$$\frac{d\alpha}{dt} = kf(\alpha) = k(1-\alpha)^n \tag{1}$$

where α is the fraction decomposed. For example, Wallouch et al. [1] investigated the carbonization of a variety of coal tar pitches using the single curve differential method [eq. (2)].

$$\ln\left[\frac{d\alpha}{dT} \frac{1}{f(\alpha)}\right] = \ln\left[\frac{A}{\beta}\right] - \frac{E}{RT} \tag{2}$$

where β is the heating rate. The parameters A and E were found to be independent of the heating rate in the range 0.4—1.7 K min^{-1} and were considered to be characteristic of the pitch materials. Both parameters increased with the softening point of the pitches, the values of E being in the range 39—97 kJ mole^{-1}. Huttinger [2], using the kinetic analysis of van Krevelen et al., observed somewhat lower values of E, of the order of 40—52 kJ mole^{-1}, again on coal tar pitch samples. The kinetics of decomposition of a wider range of organic compounds, including pitches, was investigated by Lapina et al. [3], who used the method of Freeman and Carroll to interpret the data. E values ranging from 70 to 460 kJ mole^{-1} were observed and it was suggested that these values could be correlated with the graphitizability of the cokes produced by pyrolysis.

Pitch materials are complex mixtures of hydrocarbon molecules differing in their molecular weight distributions, in the ratio of aromatic to aliphatic hydrocarbons and in the proportion of heterocyclic compounds. In the initial stages of pyrolysis, distillation of the low molecular weight species occurs, but as the temperature is raised, in addition to the increased rate of volatilization due to the progressive evaporation of larger molecules, cracking of the compounds may also occur to produce volatile fragments. These changes bring about a gradual increase in the average molecular weight of the melt. Eventually, the higher molecular weight species separate out to form an insoluble, anisotropic, liquid crystalline phase, the carbonaceous mesophase, which increases in volume fraction at the expense of the isotropic pitch [4]. This process is accompanied by a rapid decrease in the fluidity of the system as non-Newtonian flow character is imparted to it [5]. Finally, the c rbonizing system becomes entirely mesophase. This continues to lose a small amount of volatile matter before "setting" to form the coke product.

The pyrolysis process is thus exceedingly complex and many competing processes contribute to the thermogravimetric curve. Initially, the predominant mechanism of weight loss may be simply one of evaporation from a liquid surface which may be determined by the volume fraction of evaporating species or by their rate of diffusion to the surface (i.e. viscosity of the melt), but later chemical reactions occur and in the final stages volatile matter is escaping from a porous solid. Thus, although it may be possible to linearise a thermogravimetric curve for such a system by using a simple order expression, such a function is unlikely to have any real physical or chemical significance nor can the derived activation energy or pre-exponential factor be related precisely to any particular mechanistic step. Hence, in the sub-

sequent sections, they are designated as apparent values.

The multiple heating rate methods of Ozawa [6], i.e.

$$\log \beta = \log\left[\frac{AE}{Rg(\alpha)}\right]_\alpha - a - \frac{bE}{RT_\alpha} \tag{3}$$

and of Friedman [7]

$$\ln\left[\beta\frac{d\alpha}{dT}\right]_\alpha = \ln[Af(\alpha)] - \frac{E}{RT_\alpha} \tag{4}$$

are applied at a fixed value of α when the function $f(\alpha)$ and its integral form $g(\alpha)$ are considered constant and therefore no assumption need be made as to their form. It was therefore decided to apply these two methods of interpretation to thermogravimetric data from pitch materials and to compare the results with those from the two corresponding single curve methods based on the same equations, i.e. the differential single curve method of eq. (2) and the Doyle [8] method

$$\log[g(\alpha)] = \log\left[\frac{AE}{R\beta}\right] - a - \frac{bE}{RT} \tag{5}$$

In these latter two methods, $f(\alpha)$ was assumed to be of the form of eqn. (1) and

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} \text{ for } n \neq 1$$

and

$$g(\alpha) = -\ln(1 - \alpha) \text{ for } n = 1$$

EXPERIMENTAL

Ground pitch samples were contained in open silica crucibles which were suspended from one arm of a CI Electronics Mark III microbalance and enclosed in an apparatus of silica and glassware. The sample was heated in a continuous flow of dry nitrogen by means of a nichrome furnace controlled by a Stanton Redcroft linear programmer capable of linear heating rates between 0.4 and 11.0 K min^{-1}. The temperature of the sample was monitored by a Pt/Pt—13% Rh thermocouple located immediately below the crucible and was displayed continuously, along with the weight change, on an Oxford 3000 2-pen chart recorder.

The particle size of the pitch was found to have no effect on the thermogravimetric curves since the pitch is in the fused state when volatilization begins, but the coke yield was found to increase with sample weight in the region below 100 mg. This latter weight was, therefore, used in all the experiments reported here. Flow rates in the range 10—800 cm^3 min^{-1} had no apparent appreciable effect on the coke yield and the value of 50 cm^3 min^{-1} was routinely used after thorough purging of the system. Buoyancy effects were ascertained from calibration runs using inert coke samples.

The four pitches listed in Table 1 were investigated.

TABLE 1

Pitch characteristics

Pitch	Softening point (°C) (ring and ball method)	% Insoluble in		Average % weight loss on thermobalance
		Quinoline	Toluene	
Coal tar binder pitch (British Steel Corporation)	101	11.5	34.1	47.1
Coal tar impregnation pitch (British Steel Corporation)	83	2.9	19.0	56.1
Petroleum pitch A200 (Ashland)	200	0	31.2	30.4
Gilsonite (naturally occurring pitch)	143	?	?	75.3

RESULTS

For the coal tar and petroleum pitches, the final percentage weight loss decreased slightly as the heating rate increased. Therefore, in order to facilitate the analysis of the data, each curve was normalised by dividing the weight loss at any temperature by the final weight loss at that heating rate to give values of α, the fraction reacted. Normalised thermogravimetric plots for the coal tar impregnation pitch are shown in Fig. 1(a). Volatilisation occurs over the temperature range 200—600°C at the heating rates used. The binder
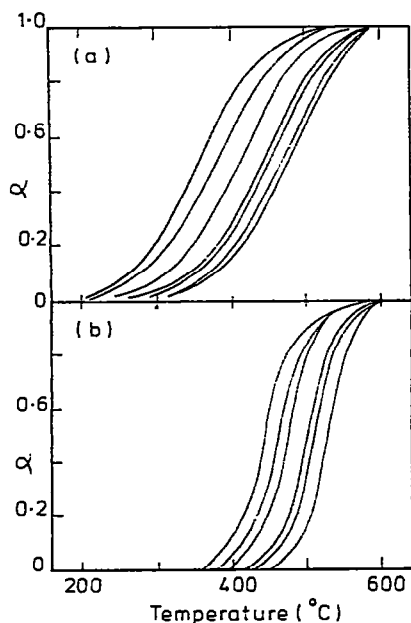

Fig. 1. Thermogravimetric curves for coal tar impregnation pitch (a) and Ashland A200 petroleum pitch (b).

pitch data were similar, but the two materials of higher softening point, Ashland A200 and Gilsonite, showed volatilization over a narrower temperature range, e.g. Fig. 1(b).

Interpretation by single-curve methods

Plots according to eqns. (2) and (5) were made assuming values of n in the range 0—2 and that value which gave the best straight lines for each system was selected. For three of the pitches, the values found to apply to both the integral and differential methods were Ashland A200 pitch $n = 1.5$, coal tar impregnation pitch $n = 1.0$ and coal tar binder pitch $n = 1.0$. Small changes in the value of n used in the analysis resulted in marked non-linearity of the plots. However, it was not possible to analyse the Gilsonite data satisfactorily by either of the single curve methods because no single value of n could be assigned to the data over the whole range of α (i.e. 0.05—0.95). For example, $n = 0.66$ would linearise the integral data up to $\alpha = 0.8$ quite well, $n = 2.0$ gave satisfactory linear plots in the high α region but not for $\alpha < 0.2$, whereas the α range 0.1—0.9 could be represented quite well by a value of $n = 1$. Figures 2 and 3 show typical differential and integral plots for the coal tar and petroleum pitches, demonstrating the tendency for slopes and intercepts to increase with heating rate. These parameters were calculated by a linear regression analysis and converted to apparent activation energies (E_a) and pre-exponential factors (A_a) using, in the case of the integral method, the values [9]

$a = 1.499$ $\quad b = 0.494$ when $10 < E/RT < 19$
$a = 2.000$ $\quad b = 0.4667$ when $18 < E/RT < 28$
$a = 2.315$ $\quad b = 0.457$ when $28 < E/RT < 50$

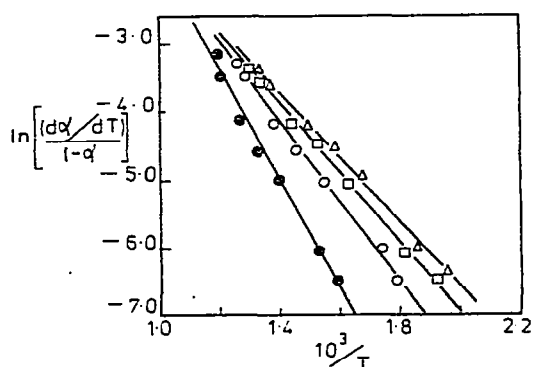Table 2 shows the variation of E_a, from both methods, with heating rate.

Fig. 2. Differential plot [eqn. (2)] of thermogravimetric data from the coal tar impregnation pitch at different heating rates. ●, 10.4 C min^{-1}; ○, 2.20 C min^{-1}; □, 1.01 C min^{-1}; △, 0.42 C min^{-1}.
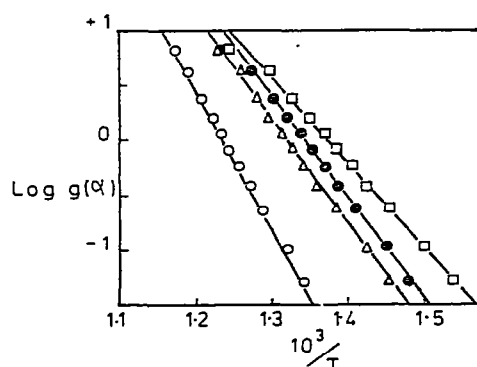
Fig. 3. Doyle plot [eqn. (5)] of thermogravimetric data from Ashland A200 pitch at different heating rates. ○, 10.4 C min^{-1}; △, 1.80 C min^{-1}; ●, 0.96 C min^{-1}; □, 0.55 C min^{-1}. 0.55 C min^{-1}.

TABLE 2

Apparent activation energies (E_a) from the integral and differential single curve methods

Heating rate	E_a (kJ mole^{-1})	
	Doyle method	Differential method
Coal tar impregnation pitch (n = 1)		
0.42	47	39
1.01	48	42
2.20	54	49
4.28	62	
6.38	65	
8.43	70	
10.4	72	72
Coal tar binder ptich (n = 1)		
0.40	51	47
1.09	58	59
2.17	60	62
4.30	65	
7.33	73	
10.2	76	82
Ashland A200 pitch (n = 1.5)		
0.55	141	125
0.96	165	156
1.80	171	169
4.53	189	
6.44	199	
10.4	223	219

The values calculated from the two methods are in good agreement. Apparent activation energies for the pyrolysis of Gilsonite varied according to the value of n chosen at any single heating rate and according to the number of points included in the regression analysis (e.g. at 0.4 K min^{-1}, E_a varies from 140 to 308 kJ mole^{-1} as n changes from 1 to 2 and at 10 K min^{-1}, the variation is from 235 to 390 kJ mole^{-1} for the same orders of reaction). Hence, since values could not be unambiguously assigned, they are not quoted in Table 2 or further discussed.

Multiple heating rate methods

Satisfactory linear plots according to eqns. (3) and (4) were obtained for all four pitches examined, over the whole range of α, and typical examples are shown in Figs. 4 and 5. Apparent activation energies at different values of α are shown in Table 3 and it is clear that both methods predict an increase in E_a with α for all materials. Figure 6 shows a plot of the apparent activation energy determined by the Friedman method against that from an Ozawa analysis at the same value of α. The plot is linear with a slope of 1.11, indicating that the Friedman method gives consistently higher values for E_a. It is also apparent from Table 2 that, for the coal tar pitches, E_a values calculated from the multiple heating rate methods show a larger variation than those obtained by single curve analyses.

TABLE 3

Apparent activation energies (E_a) from the Ozawa and Friedman multiple heating rate methods

|	α										
	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95
Coal tar inpregnation pitch											
E_a from Ozawa method (kJ mole^{-1})	59	64	74	83	85	90	94	101	119	144	164
E_a from Friedman method (kJ mole^{-1})	66	66		92		101		127		178	191
Coal tar binder pitch											
E_a from Ozawa method (kJ mole^{-1})	74	70	77	81	87	96	104	114	127	140	152
E_a from Friedman method (kJ mole^{-1})	76	77		91		117		134		157	178
Ashland A200 pitch											
E_a from Ozawa method (kJ mole^{-1})	122	128	145	155	159	165	169	182	193	215	
E_a from Friedman method (kJ mole^{-1})	127	143		171		182		207		287	
Gilsonite pitch											
E_a from Ozawa method (kJ mole^{-1})	107	135	157	168	174	176	179	182	184	191	205
E_a from Friedman method (kJ mole^{-1})	124	159		194		189		195		209	239
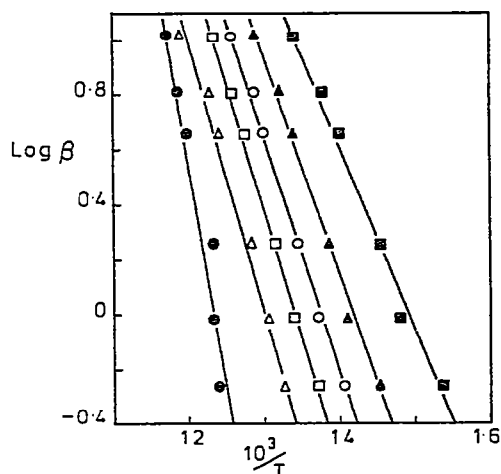
Fig. 4. Ozawa plot [eqn. (3)] of thermogravimetric data from Ashland A200 pitch. ●,
$\alpha = 0.95$;△, $\alpha = 0.8$;□, $\alpha = 0.6$;○, $\alpha = 0.4$;▲, $\alpha = 0.2$;◙, $\alpha = 0.05$.
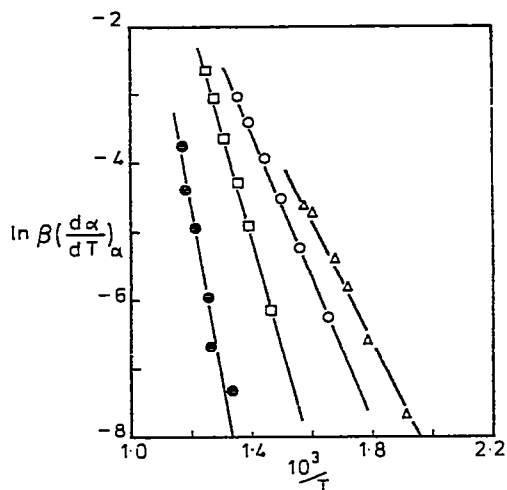
Fig. 5. Friedman plot [eqn. (4)] of thermogravimetric data from coal tar binder pitch. ●,
$\alpha = 0.95$;□, $\alpha = 0.7$;○, $\alpha = 0.3$;△, $\alpha = 0.05$.

DISCUSSION

The most striking feature of these results is that there is not a single value
of the apparent activation energy for any one pitch; the values increase with
increasing heating rate or with the value of α. Increasing the heating rate
results in the decomposition occurring at higher temperatures, when larger
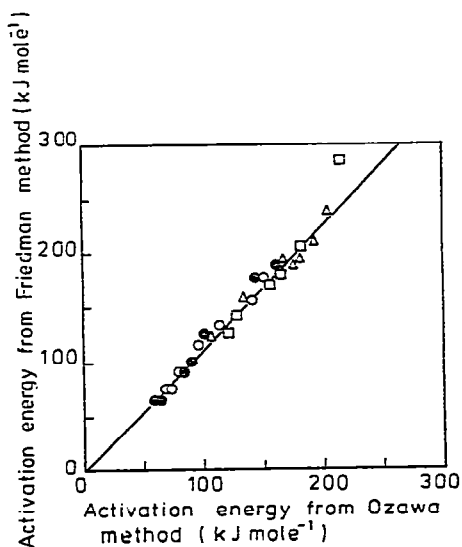molecules can evaporate and other chemical reactions may also contribute,

Fig. 6. Correlation between activation energies from Friedman and Ozawa methods of
analysis. ●, coal tar impregnation pitch; ○, coal tar binder pitch; □, Ashland A200 petro-
leum pitch; △, Gilsonite pitch.

as discussed earlier. It is suggested, therefore, that the increase in the apparent activation energy reflects this change in the nature of the predominant rate-controlling steps with increasing reaction temperature. The decomposition process is endothermic and any enhanced self-cooling effects at fast heating rates would tend to lower the observed value of E_a, as observed in studies of the decomposition of $CaCO_3$ [10].

In the multiple heating rate methods, data at high values of α are collected at higher temperatures and so the increase in E_a with α again reflects more energetic processes taking place. In a recent study of the pyrolysis of oil shale [11], using the Friedman method of analysis, it was also observed that E_a increased with percentage conversion.

A direct comparison of the multiple heating rate and single curve methods is not easy because E_a is determined from data collected over a range of temperature which varies according to the method of analysis. An attempt to do so, for the three pitches which can be described by all four methods of analysis, is shown in Fig. 7 in which the value of E_a is plotted against the midpoint of the temperature range over which that value was determined. However, this comparison is somewhat arbitrary since, if a different range of heating rates had been investigated, the average temperature at a fixed value of α would be altered, but the value of E_a from the multiple heating rate method of analysis would not. Nevertheless, it appears from this figure that, for the two coal tar pitches, the multiple heating rate methods give higher values of E_a than those obtained from single curve analysis whereas, for the Ashland petroleum pitch, all the methods give reasonable agreement.

Recently, it has been demonstrated that, where non-isothermal thermogravimetry results in variations in the apparent activation energy and pre-
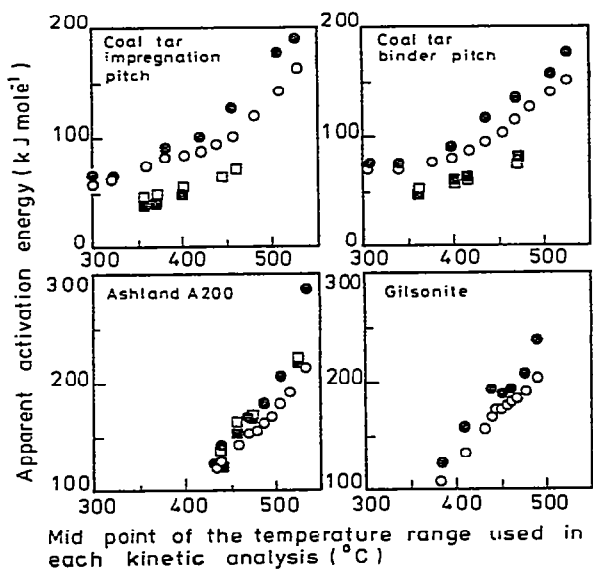

Fig. 7. Comparison of apparent activation energies from the four different methods of analysis. ●, Friedman method; ○, Ozawa method; □, Doyle method; ▪ differential single-curve method.

exponential factor, as a result of procedural changes, the data can be expressed according to the compensation effect [12,13]. Figure 8 shows a plot of log A_a against E_a for the data collected in this study, excluding the single curve methods of interpreting Gilsonite. Although there is some scatter of points, all the results from all four pitches lie close to a common line which is linear at $E_a > 60$ kJ mole^{-1}. The equation of this linear section, from a linear regression analysis is

$$\log A_a = 0.0683 \, E_a - 0.919 \tag{6}$$

where E_a is expressed in kJ mole^{-1} and A_a in min^{-1}. This compensation effect can be used to explain the relative magnitudes of the E_a values from the two pairs of methods of analysis as outlined below. The discussion will be confined to the two integral methods, but the same argument applies to the differential methods.

If the values of E_a and A_a for a given set of non-isothermal thermogravimetric curves are unaffected by heating rate, the interpretation of the data by both the Doyle intergral method and the Ozawa method should give the same values for these parameters because the two methods are based on the
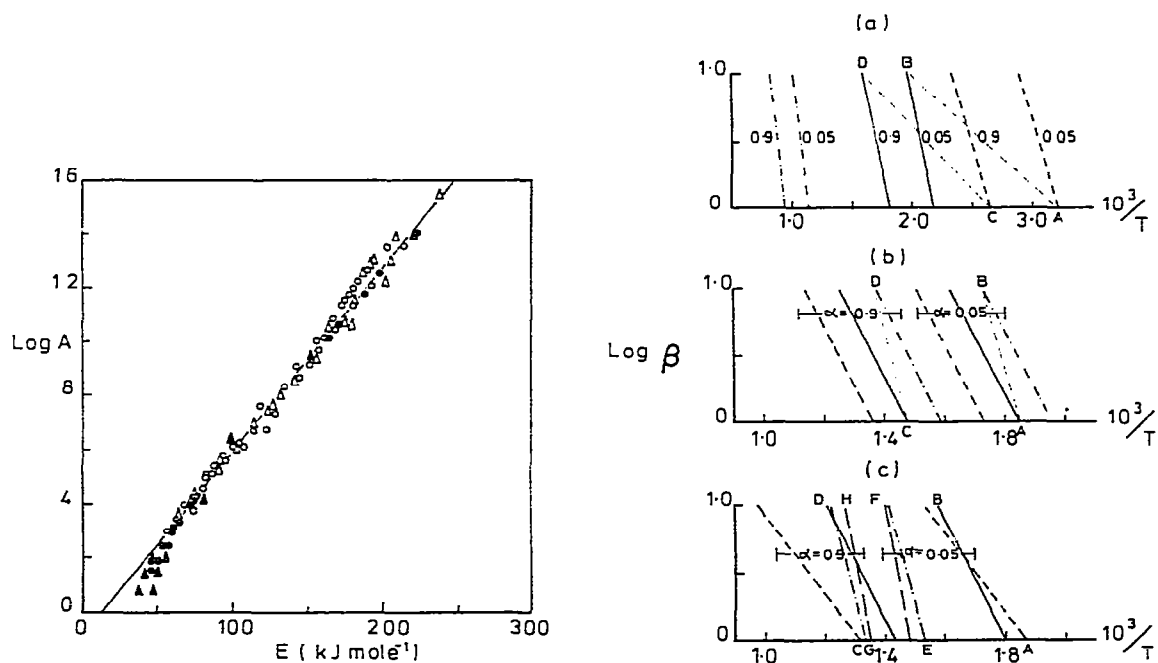

Fig. 8. Compensation plot of kinetic parameters from all four pitches. ○, Ozawa method; △, Friedman method; ●, Doyle method; ▲, differential method.

Fig. 9. Theoretical Ozawa plots calculated from eqn. (5) taking $n = 1$ and (a) log $A = 6.00$, $E = 50$ kJ mole^{-1}, — — —, $E = 75$ kJ mole^{-1}, ————, $E = 150$ kJ mole^{-1}, · — · — ·; (b) $E = 75$ kJ mole^{-1}, log $A = 4.0$, — — —, log $A = 4.5$, ————, log $A = 5.0$, · — · — ·; (c) log $A = 2.0$, $E = 50$ kJ mole^{-1} — — —; log $A = 4.3$, $E = 75$ kJ mole^{-1} ————; log $A = 9.4$, $E = 150$ kJ mole^{-1} · — · — ·; log $A = 13.0$, $E = 225$ kJ mole^{-1} — — —;

same equation. This is shown in Fig. 9(a) where three sets of data calculated from eqn. (5), assuming $n = 1$, are plotted in the Ozawa coordinates for $\alpha = 0.05$ and 0.9. Each set of data has been calculated assuming a different value of E_a (covering the range observed in this study) but a common value of A_a. Suppose now that E_a changes according to the heating rate, β, as observed in this study, but that A_a remains constant. For example, if at $\beta = 1.0$ K min^{-1}, $E_a = 50$ kJ mole^{-1} from the Doyle analysis, but at $\beta = 10$ K min^{-1}, $E_a = 75$ kJ mole^{-1} by the same method, then the corresponding points on the Ozawa plots shown in Fig. 9(a) would be A and B at $\alpha = 0.05$, and C and D at $\alpha = 0.9$. Thus, the Ozawa method would result in E_a values increasing with α, as observed here, but the values would always be lower than the corresponding single curve evaluations. Similarly, if E_a decreased slightly with heating rate when evaluated by the Doyle method, it would decrease with increasing α when assessed by the Ozawa method and always be greater in magnitude. Obviously, large decreases in E_a with increasing heating rate would result in negative E_a values observed in Ozawa's analysis, if there was no compensation effect.

If E_a is now assumed to be invariant with heating rate, but A_a is allowed to increase slightly as shown in Fig. 9(b), then the Ozawa plots would give larger E_a values than the Doyle method (e.g. lines AB and CD) and if A_a increased by a large amount, E_a again would become negative.

Figure 9(c) shows Ozawa plots of data calculated from eqn. (5) for different values of E_a, but in this case A_a has been allowed to vary with E_a according to the compensation equation, eqn. (6). It can be seen that, if over the heating range 1—10 K min^{-1}, E_a from a Doyle analysis increases from 50 to 75 kJ mole^{-1} (as observed for coal tar pitches) then the E_a values determined from an Ozawa plot at $\alpha = 0.05$ (line AB) will be slightly greater than 50 kJ mole^{-1}, and at $\alpha = 0.9$ (line CD) significantly greater than 75 kJ mole^{-1}. When E_a increases from 150 to 225 kJ mole^{-1} over the same range of heating rates, the Ozawa values of E_a at $\alpha = 0.05$ and 0.9 (lines EF and GH) are, respectively, approximately the same as those determined from single curves at 1 and 10 K min^{-1}. This was the situation with the Ashland petroleum pitch. This analysis also predicts that if E_a showed a greater variation with heating rate, e.g. from 50 to 225 kJ mole^{-1}, then the E_a value at $\alpha = 0.05$ (AF), would be much smaller than at the minimum heating rate studied, but that determined at $\alpha = 0.9$ (CH) would be slightly greater than that assessed at the maximum heating rate.

This analysis shows that the relative magnitudes of the values of E_a and A_a assessed from multiple and single heating rate methods is determined by the form of the compensation effect and the extent to which E_a varies with heating rate for a particular system.

It was mentioned earlier that the Friedman differential method of analysis always gave higher values of E_a than the Ozawa method at a comparable value of α. This is to be expected. Inspection of eqns. (3) and (4) shows that both plots can only be linear if either

$$\left(\frac{d\alpha}{dT}\right)_\alpha \simeq \text{constant}$$

or

$$\log\left(\frac{d\alpha}{dT}\right)_\alpha \propto \frac{1}{T}$$

In this study, $(d\alpha/dT)_\alpha$ is approximately independent of heating rate (i.e. T) and so it follows from eqns. (3) and (4) that the ratio of the Friedman to Ozawa apparent activation energies should be equal to 2.3 b. This value varies from 1.07 to 1.14 for the range of E/RT studied here, in good agreement with the measured ratio of 1.11 reported earlier.

It is clear from the foregoing discussion that, in this exceedingly complex system, the analysis of thermogravimetric curves is unlikely to lead to the determination of kinetic parameters which can be related to any particular rate-controlling step or particular reaction. Nevertheless, the variation of E_a with fraction reacted or with heating rate is different for each pitch (i.e. different parts of the compensation curve are covered). For any one method of analysis, the range of E_a values should reflect the previous history of the pitch material and could, therefore, be used in its characterization. For example, pitches of increasing softening point are produced by removing low molecular weight species by a heat treatment or distillation operation. The effect of this process on the Ozawa and Friedman analyses would be to shift the E_a vs. α curve to higher values of E_a. In the single curve methods of analysis, the values of E_a at each particular heating rate would also increase. For materials such as Gilsonite, which cannot be described satisfactorily by the use of a simple order function, the Ozawa and Friedman methods of analysis are undoubtedly preferable and these would require the determination of a minimum of two thermogravimetric curves at different heating rates. For other materials, which can be described by all four methods, the choice of method may depend on the information required. For routine characterisation, a single curve method of analysis involving the determination of only one thermogravimetric curve may be preferred, as in those studies reported in the introduction. If this is the case, then it is essential that the heating rate is maintained constant in view of its effect on the value of E_a. On the other hand, the Ozawa or Friedman analyses yield more information about the pyrolysis process. For example, the values of E_a determined at low α values are probably characteristic of the evaporation of the lowest molecular weight species whilst the values obtained at $\alpha > 0.85$ will be influenced more strongly by the cracking reactions.

A study of the relative merits of these and other methods of treating thermogravimetric data on these systems is continuing.

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