# ACTIVATION OF FIBROUS CHARS

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## Summary

The rates of activation by carbon dioxide of chars prepared from viscose rayon precursors treated with inorganic chlorides have been studied. The rates of reaction, activation energies and Arrhenius factors are discussed in terms of a Compensation Effect.

## Experimental and Results

Strips of viscose rayon cloth were treated reproducibly by dipping in solutions containing 5% w/w of a metal chloride plus 2.5% $NH_4Cl$, and drying, they were then carbonised (6°C/min, 4 l/min $N_2$) to the desired activation temperature (700 - 900°C). The resulting chars were activated by flowing $CO_2$ (4 l/min) for varying periods of time. Weights were recorded. In one series, $CO_2$ formed both the carbonising and activating gas; in two series the $N_2$ flow was replaced by $CO_2$ at 600°C. The object of the variations was to prepare chars of varying reactivity towards $CO_2$.

Rates of reaction (D) were calculated from the linear loss of weight with time of activation in terms of the initial weight of char ($w_o$); thus $D = dw/dt.w_o$. True rates of reaction ($dw/dt.w$) thus rose with increasing reaction. D therefore represents the initial rate of reaction (at zero activation). The results are presented in Table 1. The Arrhenius plots showed little deviation from linearity: activation energies ($\Delta E$) and Arrhenius factors (A) have been derived from these plots.

## Discussion

A considerable range of char reactivity has been achieved by the variations in the method of char preparation. In the temperature range studied the order of increasing rates of reaction of the chars is: $ZnCl_2/N_2$, $AlCl_3/CO_2$, $ZnCl_2/CO_2$, $BaCl_2/N_2$, untreated rayon/$N_2$, $CaCl_2/N_2$ (the gases indicating the carbonisation atmosphere. $\Delta E$ and A also increase in the same order.

The presence of $CO_2$ at temperatures above 600°C leads to an increase in activation rate in comparison with samples prepared in $N_2$. Assessment of the accessible surface area by heat of wetting measurements using benzene and silicone fluid showed that the presence of $CO_2$ above 600°C prevents the pore closure which otherwise occurs in an inert atmosphere. The more open char structure then shows a higher reactivity. The linearity of the Arrhenius plots implies that a single reaction - controlling mechanism persists over the temperature range studied, probably chemical rather than diffusional.

Inspection of the Arrhenius plots suggests the existence of an isokinetic temperature ($T'$) near 600°C, at which the rate of reaction $D'$ is the same for all the solids.
Thus, for a given char (activation energy $\Delta E_1$) $\ln D/D' = \Delta E_1/R\,[1/T' - 1/T]$. Alternatively, for a given series of related chars, at a given temperature $T_1$, ln D will vary linearly with $\Delta E$ according to the equation
$\ln D/D' = \Delta E/R\,[1/T' - 1/T_1]$. If now the equation is recast in the usual Arrhenius form
$\ln D = -\Delta E/RT + [\Delta E/RT' + \ln D']$, then
$\ln A = \Delta E/RT' + \ln D'$. We may thus expect that for a series of related solid/gas reactions ln A will vary linearly with $\Delta E$. This relation, the Compensation Effect (1), thus stems directly from the occurrence of an isokinetic temperature.

The present data have been tested for this phenomena by plotting ln D versus $\Delta E$ for the six solids at each of the temperatures 1023, 1073, 1123°K (Figure 1), the intercept at $\Delta E = 0$ giving $\ln D'$. The plot of ln A versus $\Delta E$ (Figure 2) also allows $\ln D'$ to be found. In both cases, linear graphs are obtained; values $D' = 6.10^{-5}$ g/g/min and $T' = 890$°K have been calculated.

The compensation effect can only occur when the reactants are closely related; in the present case the chars were all prepared from a common source, viscose rayon. The limitation on the range of rayon chars forming a common system is a matter for further work.

## Reference

(1) Exner O., *Coll.Czech.Chem.Comm.* 37, 1425 (1970).

TABLE 1. Rates of Activation by $CO_2$

| Impregnation/ Carbonisation Atmosphere | Activation Temperature °C | Activation Rate (D) mg/g/min | Activation Energy (ΔE) KJoule/mol | Arrhenius Factor (A) g/g/min |
|---|---|---|---|---|
| $ZnCl_2/N_2$ | 800<br>850<br>900 | 2.5<br>4.4<br>8.0 | 125 | $10^3$ |
| $ZnCl_2/CO_2$ | 750<br>800<br>875 | 2.0<br>5.7<br>22 | 160 | $10^5$ |
| $ZnCl_2/N_2:CO_2$ > 600°C | 750<br>800<br>850 | 2.7<br>6.6<br>15 | 170 | $10^6$ |
| $AlCl_3/N_2:CO_2$ > 600°C | 800<br>850<br>900 | 2.5<br>4.2<br>17 | 165 | $10^5$ |
| $BaCl_2/N_2$ | 750<br>850<br>900 | 2.0<br>20<br>48 | 220 | $10^9$ |
| $CaCl_2/N_2$ | 725<br>750<br>775<br>800<br>825 | 5.2<br>27<br>31<br>81<br>160 | 310 | $10^{14}$ |
| No impregnation/$N_2$ | 750<br>800<br>850 | 3.6<br>9.2<br>29 | 220 | $10^9$ |

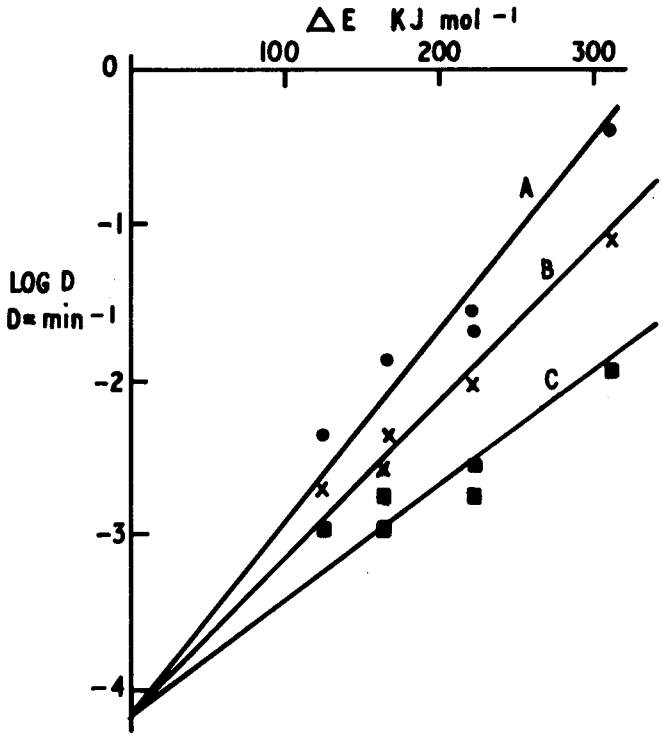


Figure 1. Variation of Log D with ΔE, constant temperature (A) 1123°K, (B) 1073°K, (C) 1023°K.

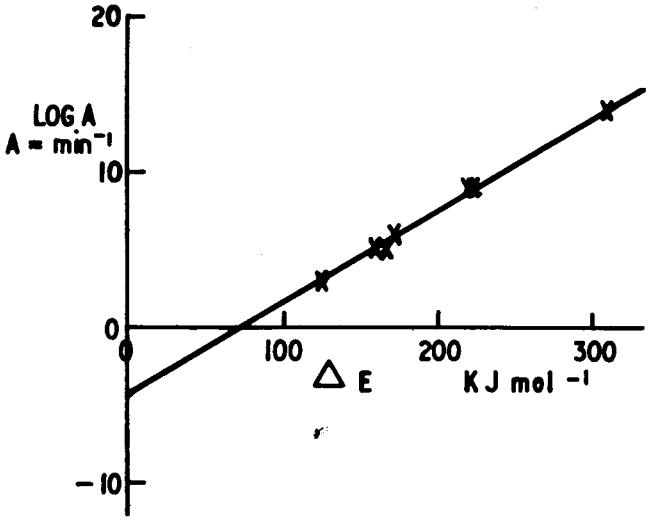


Figure 2. Variation of Log A with ΔE.