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BOND RUPTURE PROCESSES IN COAL PYROLYSIS

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The purpose of this paper is to report some preliminary findings of a study which, while primarily concerned with the kinetics of carbon crystallite growth at $T > 650^{\circ}\text{C}$, is also beginning to delineate a major route by which unpaired electrons (i.e. so-called "free radicals") form in coal chars. The results are of particular interest inasmuch as they demonstrate that skeletal C-O and C-C bond rupture processes are not - as is commonly thought - confined to the temperature region between 400° and 650°C (in which tar forms by elimination of naphthenic structures).

Experimental

Experimentally, the investigations here under discussion centre on (i) heat treatment of a coal sample in vacuo at a series of pre-selected temperatures; (ii) rapid quenching after such heat treatment; and (iii) measurement of the magnetic mass susceptibility and pure diamagnetic susceptibility of the quenched residue.

For the experiments so far completed, cleaned (-65 +200 mesh) samples of a low volatile bituminous coal (ash <0.5%; Ref. 1) were chosen. These were vacuum-carbonized at $<10^{-5}$ mm Hg and $6^{\circ}\text{C}/\text{min.}$, held at the selected final temperatures for periods varying between <5 seconds and 0.5 hr., and then rapidly cooled by external air jets. Figure 1 exemplifies a typical heating and quenching program. When the carbonized residues had attained room temperature, the furnace assembly was flooded with purified nitrogen, and the residues removed and transferred to a continuously evacuated desiccator.

Immediately prior to their use in the magnetic balance (cf. below), and always within less than 24 hrs. after preparation, samples were rapidly filled into the upper chamber of a compensated specimen holder (cf. Detail B, Figure 2) and the loaded holder re-evacuated in order to allow proper settling of the char. After 30 minutes' pumping, the holder was again flooded with purified nitrogen, removed, weighed and inserted into the vacuum chamber of the specially constructed Gouy-type balance. Sample weights were usually of the order of 1.0 gm.

The assembly in which magnetic susceptibilities were measured is diagrammatically shown in Figure 2. It consists of (i) a custom-made quartz fibre balance* (Detail A, Figure 2) suspended in a shielded vacuum chamber V; (ii) a specimen tube suspension S extending from V into an evacuated tube fitted with the necessary temperature control and measuring equipment; and (iii) a Cambridge electromagnet capable of creating fields of up to 16,000 gauss across a one-inch gap between conical pole pieces. Balance readings were taken with a cathetometer M after major weight changes had been compensated by adjusting the current to a carefully calibrated solenoid coil C. Calibration of the balance and magnet at current densities from ca. 2 to 15 amp. was carried out with pure specimens of rhombic sulphur for which $\chi = -0.490 \times 10^{-6}$ cgs units per gm. over the temperature range from 25° to -196°C.

Measurements of χ with coal chars were made at 25°C, while χ_{dia} was obtained from plots of χ vs. $1/T$, i.e. by assuming Curie's Law to be operative and extrapolating χ vs. $1/T$ to zero. To permit construction of the necessary graphs, determinations of χ were also made at -78.5°C (the sublimation temperature of CO₂) and at -196°C (the boiling point of nitrogen)**. The linearity of the resultant χ vs. $1/T$ plots, and the accuracy with which it proved possible to estimate χ_{dia} from these plots, can be gauged from Figure 3.

Individual values of χ cited below represent averages of 5 determinations which were, in turn, each replicated by measurements at several different field strengths in the range 6000 - 14000 gauss. Maximum deviation within any one set of 5 determinations was always less than 0.005×10^{-6} cgs gm⁻¹.

Experimental data so far available are summarized in Figures 4 and 5. Figure 4 shows the variation of χ and χ_{dia} with heat treatment time t_H at 500°, 600° and 750°C, while Figure 5 shows the corresponding variation of $\Delta\chi$, i.e. of $\chi_{\text{dia}} - \chi_{25^\circ}$. On the assumption that the entire paramagnetic component of χ is associated with unpaired electrons on carbon atoms, i.e. that residual mineral matter makes no significant contribution to χ , $\Delta\chi$ affords a direct measure of the "free radical" concentration.

Comments on Procedure

The temperatures at which coal samples were pyrolyzed in the present series of experiments were selected to correspond to particular points in the behaviour pattern of equilibrated specimens, i.e. of specimens which were, in each case,

* Manufactured by Worden Laboratories, Houston. The instrument used by us had a total capacity of better than 10 gms. and a sensitivity of 5 micrograms at full load.

** These temperatures were checked with a calibrated chromel/p-alumel thermocouple.

held at the final temperature for 2 hr (1). The 500°C point thus corresponds to the onset of active thermal decomposition (as evidenced by a sharp downward turn of the χ/T plot, by increasing rates of weight loss, and by an increasing d-spacing and decreasing \bar{c} -dimension of the crystallite). The 600°C point corresponds to the near-end of active decomposition. And at 750°C, marked growth of the carbon lamellae (as evidenced by large increases in their \bar{a} -dimension) is in progress.

This dependence of behaviour on temperature - and the fact that heat treatment temperatures in the present series of experiments were approached gradually - imposes an important limitation on the data shown in Figure 4. Since transient processes at temperatures below the final heat treatment temperature will take place while the coal sample approaches this final temperature, both the form and location of individual χ vs. t_H graphs within the coordinate system must be seen as extensions of changes which commence at "negative" times (i.e. to the left of the χ -coordinate in Figure 4) and at correspondingly higher χ values than the nominal initial values shown in the diagram at $t_H = 0$.

This recognition, which accounts for the inverse relationship between the "initial" susceptibility and heat treatment temperature and which also explains the fact that the χ vs t_H curve at 750°C passes through so much shallower a minimum than the 600°C curve, necessarily complicates a kinetic interpretation of the data*. But it is pertinent to note here that the problem is essentially unavoidable - that it arises from the nature of coal per se. Theoretically, the best alternative to the heating schedule chosen in this study would be shock-heating, i.e. an approach to the final temperature in minimum time. However, with diffusion control over disengagement of volatile pyrolytic products (2, 3), such a course - followed by short heat treatment periods - would produce chars containing an indeterminate residue of undischarged pyrolytic matter making an indeterminate contribution to χ . The measured value of χ would here, in other words, be meaningless.

Discussion

So far as we are aware, only H. Honda (4) has published data on the variation of χ with t_H . He does not, however, seem to have concerned himself with the detailed form of this variation - Figure 4 of his paper (4) shows results for $t_H = 15, 30, 60$ and 120 minutes only - and while the text of the paper refers to "diamagnetic mass susceptibility", it is clear that the reported values refer to the uncorrected mass susceptibility, i.e. to χ rather than χ_{dia} . For these reasons (and also because of the uncertainty attaching to the conditions under which Honda pyrolyzed his samples), the results summarized in Figures 4 and 5 cannot be viewed against an established background. But subject to the recognition that they represent initial data (and bearing in mind the limitations referred to above), they nevertheless allow of some important tentative conclusions.

*Efforts to develop graphical methods by which the necessary corrections can be interpolated seem to be meeting with some success. They will be reported in due course.

In principle, a fall in χ may be associated with either (a) the formation of unpaired electrons by any mechanism, or (b) a decrease in the size of the average aromatic area of the statistical structure unit (or lamella). (b) itself may or may not be accompanied by formation of unpaired electrons and would, if not so accompanied, cause a fall in χ by reducing the so-called London contribution to the observed mass susceptibility. Conversely, a rise in χ can be attributed to either a removal of unpaired electrons from the system (by $\sigma - \sigma$ or $\sigma - \pi$ coupling) or simple growth of aromatic lamellae. The fact that variations of χ and χ_{dia} with t_H follow virtually parallel courses (which are only displaced with respect to each other along the χ - coordinate), i.e. the relative insensitivity of $\Delta\chi$ to changes in t_H (cf. Figure 5), is in these circumstances highly significant. Bearing in mind transient processes at "negative" time values (cf. above) and noting that $\Delta\chi$ itself increases with the heat treatment temperature, it implies that, for short heat treatment periods at least, a modified (b) operates, i.e. that χ and χ_{dia} fall as a result of lamellar size reductions and simultaneous formation of unpaired electrons, but that unpaired electrons are subsequently "frozen" into the structure without actually being eliminated by pairing. In view of Figure 5, the rise in χ and χ_{dia} must clearly be ascribed to lamellar growth only.

The corollary of this conclusion is, of course, that unpaired electrons are created by rupture of $\sigma - \sigma$ bonds, i.e. by rupture of C-C and/or C-O lattice bonds.

It might usefully be observed that such an identification is in general harmony with certain other findings. It is, for example, qualitatively supported by Mrozowski and Andrew's observation (5) that the "free radical" concentrations in polycrystalline graphitized carbons can be greatly increased by prolonged grinding in inert atmospheres (or in vacuo). And it also lends support to the suggestion (6) that ultimate elimination of unpaired electrons by extended heating at $T > 650^\circ\text{C}$ can be associated with a change in the semiconductor mechanism at $650^\circ - 700^\circ\text{C}$ - from excess electron to excess "hole" conduction (7) - by postulating a progressive $\sigma - \pi$ electron interaction.

But more immediate interest attaches to the fact that conclusions derived from the data contained in Figures 4 and 5 bear directly on descriptions of the overall coal pyrolysis process.

The gross features of this process are conventionally described in terms of a 3-stage sequence which, successively, involves (i) elimination of peripheral functional groups at $T < 400^\circ\text{C}$; (ii) skeletal breakdown and reorganization between $\sim 400^\circ$ and 650°C ; and (iii) progressive growth and ordering of aromatic lamellae at $T > 650^\circ\text{C}$. It is, in other words, supposed that only the second stage involves more than peripheral reactions*.

*A recent study concerned with the kinetics of hydrogen formation at temperatures in the range $600^\circ - 800^\circ\text{C}$ has led to the conclusion (9) that rates of H-elimination are controlled by lamellar mobility and that abstraction of hydrogen from positions at the peripheries of the lamellae is the immediate precursor of crystallite growth.

In the light of evidence now available, this view requires some revision. In particular, it must now be concluded that skeletal reorganization can extend well into the third stage and that it is here connected with the elimination of residual oxygen from coal chars.

Investigations into the kinetics of water formation at temperatures in the range 650°-850°C (8) have shown that all (or almost all) oxygen lost in this range ultimately appears as water; that the reactions leading to formation of water (which must itself be regarded as a secondary or tertiary product) are all relatively fast; and that kinetic control over water formation is exerted by bond rupture processes (which, insofar as they involve non-quinoid oxygen, must partially disrupt lamellae and result in a fall in $\%$ even if no unpaired electrons are formed in the process). If it is now borne in mind that elemental hydrogen (deriving from peripheral H-atom abstraction) and water (at least partly deriving from carbonization of ether-structures and heterocyclic O-bearing aromatics) are the only products actually formed by decomposition of coal at $T > 650^\circ\text{C}^*$, association of reductions in $\%$ (and $\%_{\text{dia}}$) with oxygen-breakout at these temperatures is virtually inescapable. The fact that oxygen-breakout is, as already noted, fairly fast (and generally 90% complete within 10 minutes from the start of reaction; Ref. 8) and that $\%$ and $\%_{\text{dia}}$ undergo rapid changes at correspondingly low values of t_{H} , may be seen as additional support for such a view.

It is, however, in this connection of interest to observe that measurements of rates of water formation between 650° and 850°C indicate sequential oxygen removal by at least two reactions. If the association between oxygen elimination and changes in $\%$ here suggested is accepted, plots of $\%$ vs. t_{H} would therefore be expected to pass through at least two corresponding minima - with the second tentatively placed at $t_{\text{H}} \approx 7-8$ minutes. This point is currently being checked.

References

1. P.A. Cavell and N. Berkowitz; *Fuel*, 39 (1960), 401.
2. N. Berkowitz; *Fuel*, 39 (1960), 47.
3. H. Luther and S. Traustel; *Brennstoff Chemie*, 44 (1963), 65.
4. H. Honda; *Proc. 3rd Conf. on Carbon* (Pergamon Press, 1957), 159.
5. S. Mrozowski and J.F. Andrew; *Proc. 4th Conf. on Carbon* (Pergamon Press, 1960), 207.
6. N. Berkowitz, P.A. Cavell and R.M. Eloffson; *Fuel*, 40 (1961), 279.
7. E.A. Kmetko; *Phys. Rev.*, 82 (1951), 456.
8. Lynne F. Neufeld and N. Berkowitz; *Fuel*, 43 (1964), May.
9. N. Berkowitz and W. den Hertog; *Fuel*, 41 (1962), 507.

*The (relatively small) quantities of methane and oxides of carbon disengaged from coal chars at these temperatures appear to be formed by autohydrogenation and steam gasification of the chars (8) and therefore to be basically unrelated to the decomposition of coal per se.

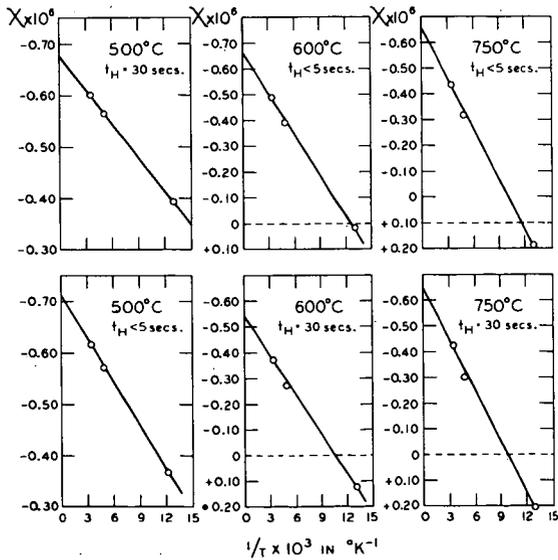
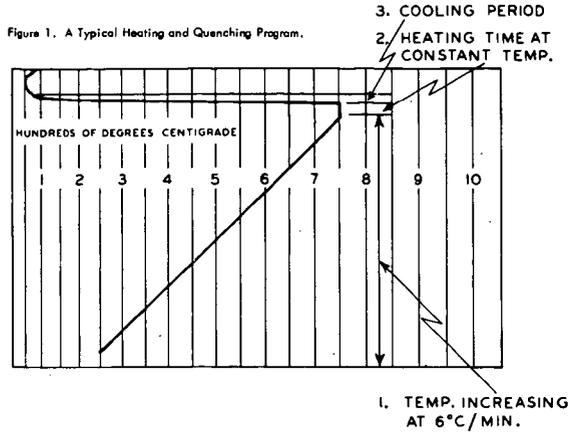


Figure 3. Some Typical Plots of X_c vs. $1/T$. ($X_{c,0} = X_c$ when $1/T = 0$.)

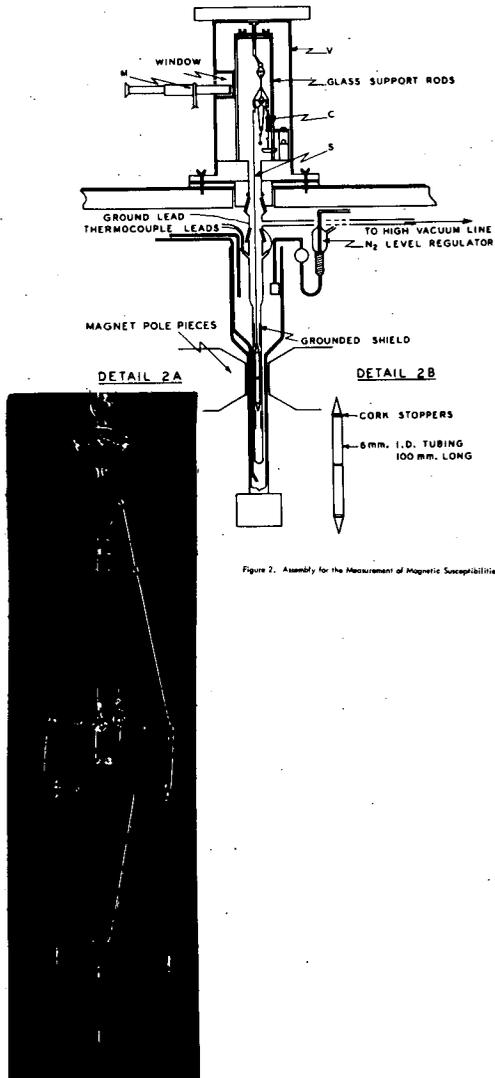


Figure 2. Assembly for the Measurement of Magnetic Susceptibilities.

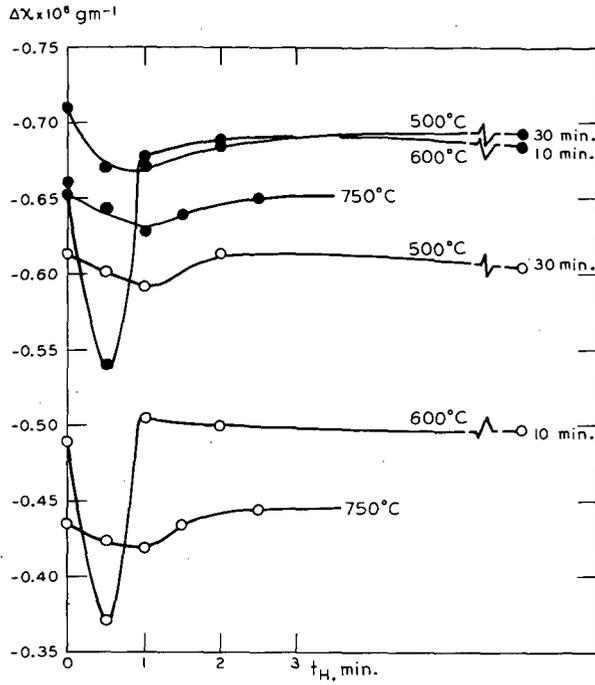


Figure 4. The Variation of Magnetic Susceptibility with Heat Treatment Time t_H . (Full circles denote χ_{dip} ; empty circles χ .)

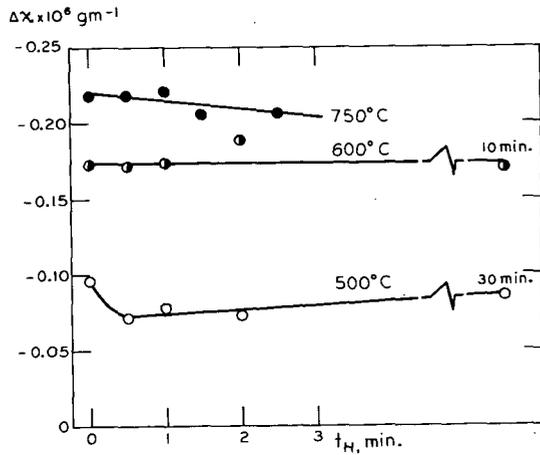


Figure 5. The Variation of χ with t_H .