

SEMICONDUCTIVITY OF HEAT-TREATED ORGANIC COMPOUNDS*

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The explanation of the semiconductivity of higher-temperature carbons in terms of interacting oxygen (ether and carbonyl) groups advanced by Weiss (1961) seems unlikely to be a general one.

A wide variety of organic substances, which may or may not contain oxygen (including, for example, polyvinylidene chloride, coals, and violanthrene), exhibit a similar pattern of development of electronic properties on heating. In each case thermal decomposition gives rise to the formation of free radicals the concentration of which rises to a maximum of 10^{19} – 10^{20} per gram and then falls to much lower values at higher temperatures. The fall in the free-radical concentration is associated with increasing electrical semiconductivity and with the progressive movement of a strong absorption edge through the infrared spectrum to longer wavelengths.

The temperature ranges in which these changes occur differ with the nature of the starting material. Decomposition of polyvinylidene chloride begins below 250 °C and the residual carbon shows a maximum electron spin resonance signal at 395 °C and marked semiconductivity at 500 °C (Winslow, Baker, and Yager 1955). The hydrocarbon violanthrene, however, when carbonized under helium exhibits a maximum electron spin resonance signal at 700 °C and is semiconducting above 750 °C (Akamatu, Mrozowski, and Wobschall 1959). In coals the changes occur at temperatures intermediate between these extremes (see, for example, Ingram 1959). Thus, organic substances containing either C, H, and Cl; C, H, and O; or C and H, all develop semiconductivity at temperatures above those of maximum free-radical concentration, but neither the carbonized polyvinylidene chloride nor the violanthrene carbons contain the conjugated ether and carbonyl oxygen groups required by Weiss' (1961) theory.

Some support for the theory of Akamatu, Mrozowski, and Wobschall (1959), that the development of semiconductivity is due to the pairing of π -electrons with the σ -electrons of broken bonds, has been obtained by Brooks and Silberman (1961), who observed an *increased* electron spin resonance signal in 650–800 °C cokes after chemical reduction with lithium in ethylenediamine. In the reduction of these materials some selective reduction of aromatic systems appears to occur, with the removal of π -electrons and the liberation of unpaired σ -electrons. With more extensive reduction, these free-radical centres may be reduced in turn. The reduction decreases the semiconductivity, and the absorption edge in the infrared spectrum is moved back to shorter wavelengths.

The onset of conductivity in carbons does not appear to be a direct function of temperature of carbonization or of degree of ring condensation of aromatic

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systems (which differs widely in the examples mentioned here), but it seems to develop when a certain proportion of the "edge" atoms or groups is removed from the condensed aromatic structures by pyrolysis (see also Waters 1961). These groups act as barriers to the movement of current carriers and in the earlier stages of pyrolysis their progressive removal produces an increasing free-radical concentration. When a certain proportion of the groups has been removed the ring clusters can approach each other more closely and, with further pyrolysis, pairing can occur between localized σ -electrons of the free radicals and π -electrons of adjacent aromatic systems. The rate of pairing must become greater than the formation of fresh broken bonds, since the overall effect is to decrease the free-radical concentration. The increasing number of holes thus produced in the π -bands leads to an increasing excess-hole type conductivity.

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