

A CHEMICAL INTERPRETATION OF THE SEMICONDUCTIVITY OF AMORPHOUS CARBONS*

By D. E. WEISS†

It is well established by the detailed studies of Mrozowski and his school (1952, 1959; Kmetko 1951) and others (e.g. Hirabayashi and Toyoda 1952) that the electrical conductivity of different chars and carbons prepared by carbonization in the temperature range 600–800 °C is that of a *p*-type semiconductor which steadily reverts to a more metallic type conductivity at higher temperatures of carbonization. It is also established that the onset of electrical conductivity at carbonization temperatures of 600–700 °C is accompanied by a rapid loss in free electron spins as measured by electron spin resonance. This was accounted for by assuming "that above 700 °C the electrons which disappear from the π band are the same which become trapped by the spin centres and destroy their ability to show the paramagnetic absorption" (Akamatu, Mrozowski, and Wobschall 1959). However, no satisfactory reason could be advanced as to why the electrons should jump into the σ -traps only above a certain temperature.

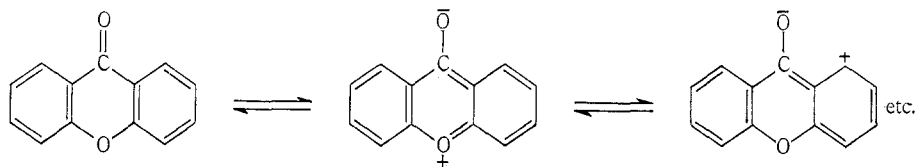
It is possible to account for these facts in another way. X-Ray studies have shown that a considerable growth in the size of the layer planes occurs at carbonization temperatures exceeding 700 °C so the loss in free spins could be due to their combination during this growth. It is also well established that the chemical character of a carbon markedly changes at carbonization temperatures exceeding 700 °C. At lower temperatures the carbon is acidic due to chemisorbed acidic oxygen structures which decompose from 400 to 700 °C. Above 700 °C the carbon is predominantly basic. The basicity reaches a maximum at about 750 to 800 °C and becomes small at temperatures exceeding 1000 to 1200 °C. The oxygen content of a carbon falls from a value of about 2–3% when prepared at 800 °C to less than 1% at temperatures above 1000 °C. Recent studies have shown that at least some, if not all, of this oxygen is present as carbonyl and ether oxygen. Some of the ether oxygen is thought to be associated with the basicity of the carbon in chromene-like structures (for a recent review see Garten and Weiss 1957).

Because a carbonyl is an electron acceptor and an ether oxygen is an electron donor some electronic interaction between the two is to be expected within the

* Manuscript received October 4, 1960.

† Division of Physical Chemistry, C.S.I.R.O. Chemical Research Laboratories, Melbourne.

carbon. The simplest instance of this is xanthone which to some extent exists, even at room temperatures, as the following dipole :



This tendency to revert to a more aromatic structure is probably responsible for the extraordinary thermal stability of xanthone. At 850 °C this is reported to give a 10% yield of dibenzofuran (Orlow and Tistschenko 1930). An analogous interaction in carbons whose aromatization has proceeded far enough for through-conjugation to develop would give rise to the observed *p*-type semiconductivity since the proportion of the structure ionized, and hence the conductivity of the polymer, would be a function of temperature. As oxygen is lost during carbonization at temperatures exceeding 1000 °C these structures are destroyed and a less temperature-dependent conductivity arises. Thus the carbonyl group functions as an electron trap in a similar fashion to the carboxyl of a xanthene organic semiconducting polymer described recently (McNeill and Weiss 1959).

References

- AKAMATU, H., MROZOWSKI, S., and WOBSCHALL, D. (1959).—"Proceedings Third Biennial Carbon Conference, Buffalo." pp. 135-45. (Pergamon Press: New York.)
- GARTEN, V. A., and WEISS, D. E. (1957).—*Rev. Pure Appl. Chem.* **7**: 69-122.
- HIRABAYASHI, H., and TOYODA, H. (1952).—*J. Phys. Soc. Japan* **7**: 337-8.
- KMETKO, E. A. (1951).—*Phys. Rev.* **82**: 456.
- MCNEILL, R., and WEISS, D. E. (1959).—*Aust. J. Chem.* **12**: 643-56.
- MROZOWSKI, S. (1952).—*Phys. Rev.* **85**: 609. (Errata *Phys. Rev.* **86**: 1056 (1952).)
- MROZOWSKI, S., CHABERSKI, A., LOEBNER, E. E., and PINNICK, H. T. (1959).—"Proceedings Third Biennial Carbon Conference, Buffalo." pp. 211-22. (Pergamon Press: New York.)
- ORLOW, N. A., and TISTSCHENKO, W. W. (1930).—*Ber. dtsch. chem. Ges.* **63**: 2948-51.