ESR STUDY OF THE KINETICS OF CARBONIZATION

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I. Introduction

There have been a number of attempts to relate the stable free radicals observed by electron spin resonance (ESR) to the mechanism of the thermal transformation of organic materials to pitch, coke, and carbon. For example, ESR has been measured as a function of heat treatment temperature (HTT) for many materials, and efforts have been made to correlate the data with the ultimate carbonization behavior.[1] Specific radical intermediates which are suggestive of different types of thermal reactions have also been identified.[2] However, none of the previous work has tried to utilize the ESR technique to study the kinetics of the transformation of pitch to coke. The purpose of this study was to determine the free radical concentration and characteristics as a function of time at various heat-treatment temperatures, and to relate the data to both kinetic and constitutional parameters for both a well-graphitizing and a poorly-graphitizing material.

II. Experimental

A. Sample Preparation

The two starting materials used were a well-graphitizing petroleum pitch derived from catalytic cracking and a poorly-graphitizing ethylene tar pitch. The heat treatments were performed in an inert atmosphere using three to four gram samples of pitch in ceramic boats. The heat-treatment temperature was accurately monitored by a thermocouple placed at a fixed position in a specially constructed aluminum sample-boat holder.

B. ESR Measurements

Weighed, evacuated samples (1-10 mg) were measured in a 10 GHz superheterodyne spectrometer at room temperature. Power levels were kept below 100 microwatts to avoid saturation. All the signals were assumed to be Lorentz-shaped and "effective" spin concentrations, N_{eff}, were calculated from $S_F^2 D$, where S_F is the peak-to-peak linewidth and D is the peak-to-peak amplitude of the derivative curve. A ruby crystal was used as a secondary standard, $CuSO_4 \cdot 5H_2O$ as a primary standard, and Curie's law was assumed.

III. Experimental Results

A. Spin Concentrations (N_{eff})

Spin concentrations were measured for the petroleum pitch samples as a function of time at heat-treatment temperatures of 400°C, 430°C, 460°C, and 490°C and for the ethylene tar pitch at 400°C, 430°C, and 460°C. The experimental results obtained for the 400°C heat-treated materials are plotted in Figure 1. The N_{eff} values are seen to increase regularly with increasing heat-treatment time for each material. The poorly graphitizing pitch, however, shows a more rapid rate of free radical development than the well-graphitizing pitch. Similar differences in rate were found for each of the subsequent heat-treatment temperatures. The data do not seem to obey simple first order kinetics.

B. Linewidth (S_F)

Figure 2 shows plots of the variation of ESR linewidth with heat-treatment time for the petroleum pitch at each of the four reaction temperatures. The decrease in linewidth with time is consistent with a line-narrowing mechanism which is related to an increase in both free radical size and concentration.

C. Correlation of ESR Data with Molecular Constitutional Parameters

In Figure 3, the N_{eff} data at all temperatures are plotted versus the atomic C/H ratios measured for each material. It is significant that all of the data for a given material fall on a single curve. Of equal significance are the different relationships between N_{eff} and C/H ratio for the two materials. The higher free radical content for a given C/H ratio in the ethylene tar pitch is consistent with a higher average molecular weight and a lower degree of ring fusion in this more poorly-graphitizing pitch.

D. Free Radical Kinetics During Mesophase Formation

There has been some question about the importance of dehydrogenation during the formation of mesophase in pitch. Figure 4 contains plots of both C/H ratio and N_{eff} versus the pyridine insolubles content during mesophase development at both 400°C and 430°C for the petroleum pitch. The results show that the change in solubility is due to an increase in molecular weight resulting from aromatic dehydrogenation. The correlation between N_{eff} and P.I. content indicates that the stable free radicals are concentrated in the higher molecular weight components of the mesophase pitch.

IV. Conclusions

Our results are consistent with the following conclusions concerning the role of free radicals in carbonization.

(1) The free radical characteristics as measured by ESR, (N_{eff} and S_F) correlate with the changes in molecular constitution which accompany the dehydro-

genative polymerization process during carbonization.

(2) The ESR kinetic results obtained for the stable free radicals in carbonization appear to be related to the ease of graphitizability of the starting material.

(3) The concentration of stable free radicals during carbonization seems to be a direct function of molecular weight.

(4) The correlation of all of the free radical parameters with chemical kinetic data for the carbonization reactions, supports the contention that free radical formation is the rate-controlling step in the carbonization process.

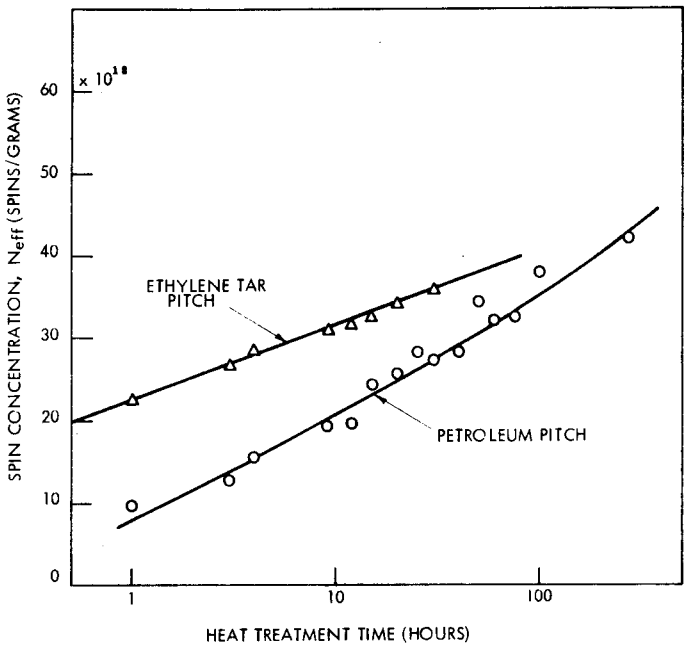

Figure 1. Effective Spin Concentration (N_{eff}) vs. Heat Treatment Time at 400°C; △ Ethylene Tar Pitch, and ○ Petroleum Pitch.

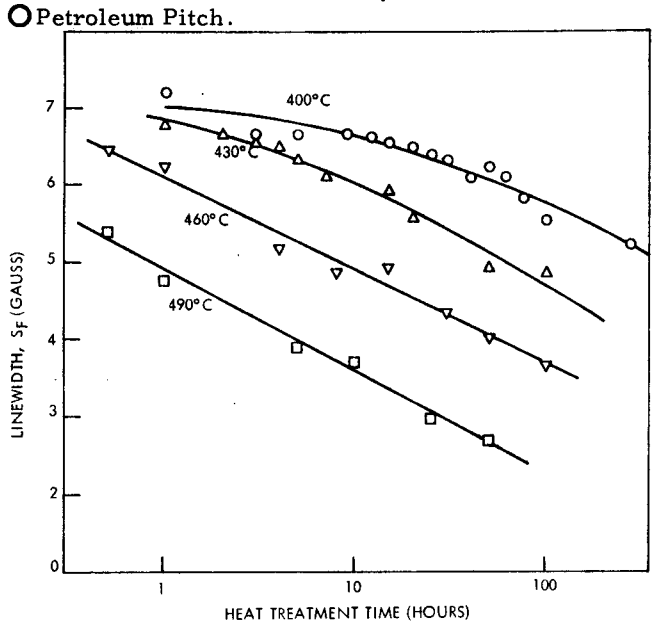

Figure 2. Linewidth (S_F) vs. Heat Treatment Time at 400°C, 430°C, 460°C, and 490°C for the Petroleum Pitch.

V. Acknowledgments

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References

1. L. S. Singer, Proceedings of the Fifth Carbon Conference, Volume II (1963).

2. I. C. Lewis and L. S. Singer, Carbon 7, 93 (1969).

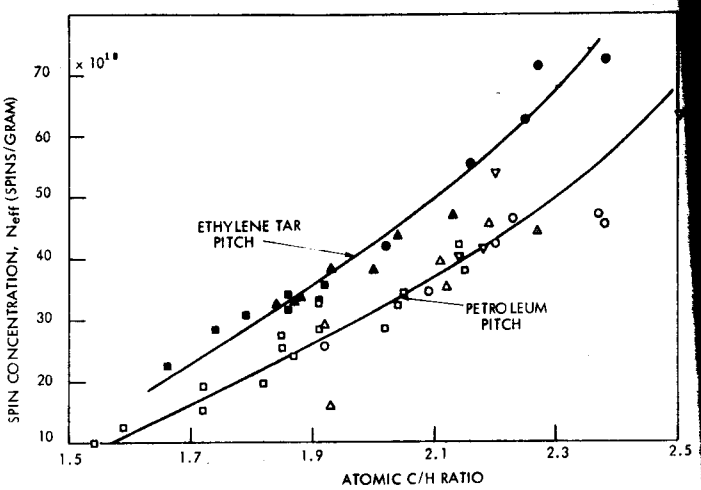

Figure 3. Effective Spin Concentration (N_{eff}) vs. Atomic C/H Ratio for Ethylene Tar Pitch and Petroleum Pitch Heat Treated at Various Temperatures. Petroleum pitch: □ 400°C, △ 430°C, ○ 460°C, and ▽ 490°C; Ethylene Tar Pitch: ■ 400°C, ▲ 430°C, and ● 460°C.

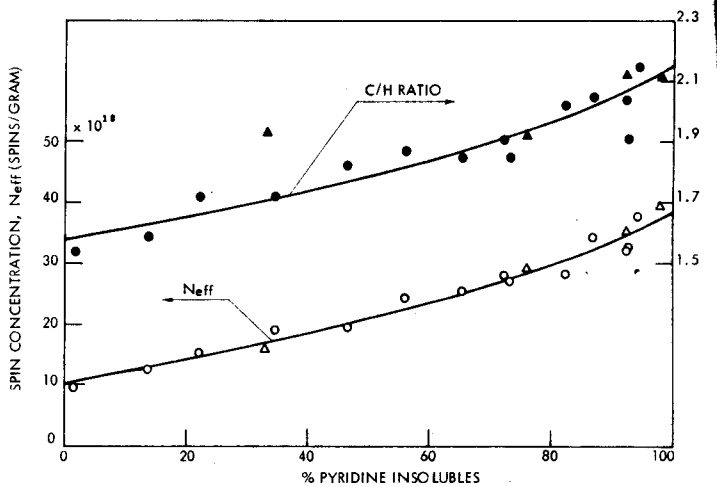

Figure 4. Effective Spin Concentration (N_{eff}) and Atomic C/H Ratio vs. % Pyridine Insolubles for the Petroleum Pitch Heat Treated at 400°C and 430°C; ○ ● 400°C; △ ▲ 430°C.