INFRA-RED STUDY OF STRUCTURAL CHANGES DURING THE PYROLYSIS OF A PHENOL-FORMALDEHYDE RESIN

K. OUCHI
Division of Coal Research, CSIRO, Chatswood, New South Wales, Australia
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Abstract—On pyrolysis of a phenol-formaldehyde resin at temperatures up to 700°C there was no change in the infra-red spectrum below 300°C but above this temperature the hydroxyl absorption began to decrease. This and other changes indicated the formation of diphenyl ether type linkages between benzene nuclei with the elimination of water. Above 400°C the changes which occurred in the spectra suggested that dibenzyl ether structures decompose to benzylphenyl ethers and that xanthene or diphenylene oxide type oxygen groups are probably formed. Some methylene bridges decompose, forming carbonyl or methyl groups, which reach a maximum content at 500-550°C. Above 500°C the diphenyl ether type linkages decompose rapidly and poly-substitution of benzene nuclei increases. From 600°C onwards the aromatic hydrogen also begins to be eliminated and the spectra become structureless, perhaps because of the condensation of aromatic nuclei. The oxygen left at this stage may be present as inner-ring oxygen, as in diphenylene oxide.

1. INTRODUCTION

The pyrolysis of phenol-formaldehyde resins has been extensively studied by measurements of diamagnetic susceptibility, electrical conductivity and X-ray diffraction, as well as by analysis of the gaseous decomposition products.(1-6) Changes in the infra-red spectrum of a phenol-formaldehyde resin during pyrolysis were reported by CZUCHAJOWSKI,(7) though without detailed discussion. The present paper provides additional support for the hypothetical structural changes previously described by OUCHI and HONDA.(8)

2. EXPERIMENTAL

The phenol-formaldehyde resin was synthesized using an equimolecular mixture of phenol and formaldehyde (36% solution) with ammonium hydroxide as catalyst. It was heated at 100°C in vacuo overnight and ground to a fine powder. Each carbonization was carried out in vacuo with a temperature rise of 2°C/min.

Infrared spectra were obtained using the KBr pellet technique and a sample concentration 0.5%. Quantitative estimations were made using a base-line method and correcting to the original-resin weight basis to compensate for concentration effects due to loss of volatiles during pyrolysis.

In the hydriodic acid treatment for cleaving an ether-type linkage 1 g of sample and 10 g of hydriodic acid solution (57%) were refluxed for 4 hr; the products were filtered, washed with water, and dried in a vacuum oven at 100°C.

Replacement of alcoholic hydroxyl groups by chlorine was carried out by treating 1 g of sample with 2 g of phosphorus pentachloride in 50 cm³ of carbon tetrachloride, and refluxing and stirring for 6 hr. After reaction the products were filtered, washed with carbon tetrachloride, and dried in a vacuum oven at 100°C.

Replacement of alcoholic hydroxyl groups by bromine was carried out by treating 1 g of sample with 10 g of hydrobromic acid (48% solution) and 1 g of conc. sulphuric acid, and refluxing for 6 hr. After addition of water, and filtration, the residue was washed well with water and dried in a vacuum oven at 100°C.

Reduction by sodium metal in liquid ammonia was carried out as follows: A 250 cm³ three-necked flask was cooled with dry ice, and ammonia gas was condensed in it. About 0.5 g of sodium
metal was dissolved in the liquid ammonia (about 100 ml) and then 1 g of sample was added under nitrogen atmosphere. The mixture was stirred for 3 hours and the flask then allowed to warm up to room temperature with addition of dry ammonium chloride to decompose the excess sodium metal. After evaporation of the ammonia the residue was washed with water, filtered, and dried in a vacuum oven at 100°C.

3. RESULTS

The changes in the infra-red spectra of the resin during the carbonization process are shown in Fig. 1 and explained below.

3.1 OH stretching vibration near 3400 cm⁻¹

The intensity of this band (see Fig. 2) decreases with increase in temperature and there is an inflexion indicating a more rapid elimination of OH groups above about 350°C. This corresponds to the onset of evolution of water as determined previously by gas analysis⁶ and indicates the start of the elimination of the phenolic OH groups.

3.2 Aromatic and aliphatic stretching vibration near 3000 to 2800 cm⁻¹

Figure 3, which gives the temperature variation of the ratio of the optical densities of the bands near 3000 and 2900 cm⁻¹, indicates a small relative decrease of aromatic hydrogen up to 400°C followed by a sharp increase at higher temperature. The latter corresponds to the onset of evolution of methane and hydrogen reported previously⁶ and is probably due to breaking of methylene bridges.

3.3 Bands at 1660 to 1630 cm⁻¹

The original resin has an absorption peak at 1637 cm⁻¹ which is eliminated on heating to 300°C and is absent from the spectrum of the resin.

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Fig. 1. Changes produced in infra-red spectra by heat treatment of phenol formaldehyde resin.
synthesized using hydrochloric acid as catalyst (Fig. 1). This suggests that it may correspond to the N–H vibration of ammonia used as catalyst.

Above 400°C another band at about 1660 cm\(^{-1}\) begins to appear. This is unaffected by treatment with bromine in chloroform, but the intensity of the band is reduced significantly by reduction with sodium metal in liquid ammonia. This suggests that the band may be due not to double bonds but to carbonyl groups. The variation of optical density with pyrolysis temperature is shown in Fig. 4. The maximum occurs at 500°C.

3.4 Aromatic ring vibration bands near 1600 and 1500 cm\(^{-1}\)

The intensities of these absorption bands are known to vary widely from one compound to another, and no reliable significance can be attributed to variation of optical density, especially for the 1500 cm\(^{-1}\) band. But the variation of the optical density of the 1600 cm\(^{-1}\) band is similar to
**Fig. 4.** Variation of 1660 cm$^{-1}$ and 1385 cm$^{-1}$ bands caused by heat treatment.

- × 1660 cm$^{-1}$; ○ 1385 cm$^{-1}$.

**Fig. 5.** Variation of optical density of 1320 cm$^{-1}$ band and its band position caused by heat treatment.

- × Optical density of 1320 cm$^{-1}$ peak;
- ○ Wave number at maximum absorption.
those of the 3000 cm\(^{-1}\) band and the aromatic CH out-of-plane vibration.

3.5 Aliphatic deformation vibration bands between 1500 and 1370 cm\(^{-1}\)

The original resin gives three distinct bands in the 1500-1400 cm\(^{-1}\) region and none in the \(-\text{CH}_3\) symmetrical-vibration region (1370-1380 cm\(^{-1}\)). The strongest band is at 1474 cm\(^{-1}\) and the others are at 1482 and 1440 cm\(^{-1}\). The band at 1474 cm\(^{-1}\) may correspond to \(-\text{CH}_2-\) bridges and that at 1440 cm\(^{-1}\) to the \(-\text{CH}_2-\) adjacent to oxygen, as in primary alcoholic (\(\text{CH}_2\text{OH}\)) or dibenzyl ether linkages (\(-\text{CH}_2-\text{O}-\text{CH}_2-\)). But for reasons to be discussed later in the present paper the presence of primary alcoholic \(-\text{CH}_2\text{OH}\) groups is unlikely and the band is therefore assigned here to dibenzyl ether structures.

These bands begin to change above 400°C. The band at 1474 cm\(^{-1}\) decreases in intensity and a new and strong band appears at 1465 cm\(^{-1}\). The other bands (1482 and 1440 cm\(^{-1}\)) disappear. At the same time a weak 1385 cm\(^{-1}\) band begins to appear (Fig. 4), corresponding to a \(-\text{CH}_3\) symmetrical-deformation vibration. These observations probably confirm that the significant changes occur at methylene bridges.

3.6 C=O stretching and OH deformation vibrations near 1320 and 1200 cm\(^{-1}\)

The intensity of these bands arises mainly from phenolic hydroxyl groups in the original resin. The variation of optical density of the bands with pyrolysis is shown in Figs. 5 and 6. As carbonization temperatures are increased above 300°C the 1320 cm\(^{-1}\) band begins to shift to lower wave

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**Fig. 6.** Variation of optical density of 1200 cm\(^{-1}\) band and its band position caused by heat treatment.

- X Optical density of 1200 cm\(^{-1}\) peak
- O Wave number at maximum absorption
numbers and that at 1200 cm\(^{-1}\) to higher frequency, indicating a change of the nature of the oxygen groups. The optical density of the 1200 cm\(^{-1}\) or 1320 cm\(^{-1}\) bands then decreases. If these bands come from hydroxyl groups they should correlate with the variation of the stretching vibration at 3400 cm\(^{-1}\); however, the latter shows a continuous decrease. Production of a new structure such as xanthene or diphenylene oxide is suggested according to the reaction (cf. xanthene, 1300 and 1280 cm\(^{-1}\);\(^{(8)}\) and diphenylene oxide, 1196 cm\(^{-1}\);\(^{(9)}\)):

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{O} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

3.7 The band near 1256 cm\(^{-1}\)

This band in the spectrum of the original resin may be a part of the OH\(^{-}\) deformation and CO\(^{-}\) stretching vibrations. The corresponding increase in intensity (Fig. 7) is rapid above 400°C and levels off to a maximum at 500°C. Reaction of sodium metal in liquid ammonia gives a reduction of intensity, indicating cleavage of diphenyl ether type linkages and providing strong evidence for the occurrence of the following reaction during carbonization:

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{O} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

This linkage disappears rapidly above 500°C.

3.8 The 1098 cm\(^{-1}\) band

The spectrum of the original resin includes a fairly strong band at 1098 cm\(^{-1}\), the intensity of which was reduced by treatment with hydriodic acid (Fig. 8) although the spectrum was not affected by halogenation reactions. This evidence suggests that the 1098 cm\(^{-1}\) band is due to the presence of aliphatic ether. As indicated in Fig. 7, the band decreases steadily in intensity with increase in heat-treatment temperature, especially from 400°C, and disappears at 500°C.

3.9 Aromatic CH out-of-plane vibrations between 900 and 700 cm\(^{-1}\)

In the spectrum of the original resin there are prominent bands at 828 and 760 cm\(^{-1}\). The former is consistent with the presence of 1:4—or 1:2:4—substitution and the latter with 1:2—or 1:2:6—substitution. A marked increase was observed in the intensity ratio of the 880 and 828 cm\(^{-1}\) bands to the 760 cm\(^{-1}\) band above 500°C particularly, indicating that a rise in temperature increases the degree of substitution in the aromatic groups, and that this increase is more rapid above 500°C.
4. DISCUSSION

The essential features of the structure of the original phenol-formaldehyde resin are probably as follows:

\[
\text{\text{OH}} \quad \text{with some cross-linking between the linear structures (i.e. some aromatic rings possess 1:2:4:6 tetra substitution); there is also a small content of } -\text{CH}_2-\text{O-ClI}_2- \text{ groups. Up to 300°C this structure does not change, but at higher temperatures water begins to be evolved.}^{(6)} \text{ These effects can be explained on the basis of three alternative assumptions:}
\]

(a) Dehydration between two phenolic hydroxyl groups, as indicated in equations (1) and (2) above, with production of diphenyl ether type linkages (open and cyclic) between benzene nuclei.

(b) Dehydration between phenolic hydroxyl groups and methylene bridges. The intensity of the methylene band at 1474 cm\(^{-1}\) decreased and another strong band at 1465 cm\(^{-1}\) appeared in a 400°C sample. This is supporting evidence for reaction (4), though the evolution of methane, hydrogen and carbon monoxide is not marked at this temperature.

(c) Dehydration between phenolic hydroxyl groups and aromatic hydrogen. The slight decrease of aromatic hydrogen between 300 and 400°C (Fig. 3) suggests that this reaction takes place to some extent.

Of these three assumptions, (a) appears to be the most tenable. Reactions (b) and (c) are not known to occur.

OUCHI and HONDA\(^{(6)}\) have shown that evolution of gas—methane, hydrogen, carbon monoxide and water vapour—is most marked between 400 and 600°C and the infra-red spectra confirm that extensive structural changes occur. The evolution of water vapour indicates that the reaction taking place in the preceding stage is continuing; this appears to produce xanthene or diphenylene oxide type inner-ring oxygen linkages as well as the open diphenyl ether type. The latter structures decompose suddenly from 500°C upwards. Aliphatic ether structures such as \(-\text{CH}_2-\text{O-CH}_2-\) decompose at temperatures of 400°C and above, and almost disappear at 500°C.

It was suggested previously\(^{(6)}\) that one methylene bridge in 7:5 reacts with water to give carbon monoxide, another decomposes to form methane and the rest remain in the carbon. The elimination of methylene bridges was considered to involve the following reactions:

\[
\begin{align*}
\text{-CH}_2- + \text{H}_2\text{O} & \rightarrow \text{CO} + 2\text{H}_2\text{O} \\
\text{-CH}_2- + \text{H}_2 & \rightarrow \text{CH}_4
\end{align*}
\]

As intermediate stages of (5) and (6) the following reactions are now proposed:
The simultaneous appearance of a weak carbonyl band at 1660 cm\(^{-1}\) (cf. \(v_{C=O}\) at 1667 cm\(^{-1}\) in anthrone\(^{(10)}\)) and a methyl band at 1385 cm\(^{-1}\) provides some support for these suggestions.

At 500°C and above, polycrystallization of the benzene nucleus corresponding to changes in intensity ratio of the 880 cm\(^{-1}\) band to 760 cm\(^{-1}\) band begins to increase, with elimination of aromatic hydrogen. However, measurements of density\(^{(1,3)}\) indicate that growth of condensed planar aromatic structures does not take place significantly below 600°C, and the increase of substitution may be attributed to the formation of, for example, fluorene-type nuclei or other disturbed network structure.

From about 700°C the dehydrogenation of aromatic hydrogens is accompanied by increased aromatization of the whole structure. Even at this stage one oxygen atom for every fourteen carbon atoms still survives in the residual carbon\(^{(1,4)}\) and, from the strong absorption at 1300–1200 cm\(^{-1}\) in the 600°C sample, it may be inferred that this oxygen is accounted for by xanthene or diphenyloxide type inner-ring oxygen. If the structure has an elementary composition corresponding to \(C_{14}H_{10}O\); the elementary analysis of the char shows exactly the same composition.\(^{(1,4)}\) The 700°C sample has a composition \(C_{14}H_{5.2}O_{1.2}\), so that there is a loss of about five hydrogen atoms per unit between 600 and 700°C. Perhaps half of these come from methylene bridges and the remainder from aromatic hydrogen. This could be checked by substituting deuterium for methylene-bridge or aromatic hydrogens.

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