

CARBONIZATION OF AROMATIC COMPOUNDS AND A STUDY OF THE SURFACE GROUPS ON THE RESULTING COKES

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Attempt has been made to carbonize aromatic compounds containing carboxylic, carboxylic anhydride and phenolic functional groups in the presence of aluminium chloride as catalyst to establish whether the functional groups of the original compounds exist as such on the surfaces of the resulting cokes or if they change during carbonization. The acidities of the cokes were determined with aqueous sodium hydroxide and alcoholic potassium hydroxide. The acidities found in alcoholic medium were higher than that in the aqueous medium, which supported the view that the functional groups of the original compounds might have changed (at least partly) during carbonization and some new groups probably keto-enol had been formed on the surfaces of cokes. Carboxylic or carboxylic anhydride groups if they were present, would have been neutralized to a substantially equal extent in the aqueous and nonaqueous media.

INTRODUCTION

Carbonization of pure organic compounds has been a matter of quite interest for the past few years. Much work in this field has been devoted to studying the carbonization reactivities of the organic compounds and the graphitizability and microscopic structure of the resulting cokes. Kinney and Del Bel [1] studied the carbonization of benzene, naphthalene, anthracene, chrysene and pyrene in the gas phase in the temperature range of 800–1100° and found that anthracene was carbonized most easily whereas benzene was the most difficult to carbonize. Milliken [2] carbonized a number of aromatic hydrocarbons and some oxygenated derivatives such as benzoic acid, naphthoic acid and phthalic acid etc. The carbonization was done in the liquid phase in the temperature range of 475–600° in a steel bomb under the vapour pressure of the compound being carbonized. He found that the structure of the starting material was of fundamental importance in deciding the character of the resulting coke.

Carbonization in the presence of alkali metal [3] and aluminium chloride [4,5] as catalysts have also been performed. The yield and the nature of the coke depended on the nature of the compound being carbonized and the catalyst used.

The purpose of the present work was to carbonize aromatic compounds containing carboxylic, carboxylic

anhydride and phenolic functional groups in the presence of aluminium chloride as a catalyst, and to investigate the neutralization behaviour of the cokes thus formed. Less attention has been paid to such type of study in the past and it would be important to know whether the original functional groups remain on the surfaces of cokes (at least in small proportions) or if they are totally evolved at the high temperature during carbonization.

It was hoped thereby to produce cokes having the clear characteristics associated with the functional group present in the starting material.

EXPERIMENTAL

Carbonization of Aromatic Compounds. The organic compounds chosen for carbonization were naphthalene (Microanalytical reagent grade obtained from British Drug House Ltd.), 1-naphthoic acid (Chemical reagent grade obtained from British Drug House Ltd.), 1-naphthol (Analytical reagent grade obtained from Koch-Light Lab. Ltd.) and 1,8-naphthalic anhydride (Chemical reagent grade obtained from Chemical Co. Ltd.).

The carbonization procedure was similar to Mochida *et al.* [4]. The organic compound was mixed thoroughly with 0.1 mole ratio of powdered anhydrous aluminium chloride under nitrogen and was carbonized in a pyrex tube 30 cm long and 3 cm in dia provided with a reflux conden-

ser under an atmosphere of flowing nitrogen. The heating apparatus consisted of a resistance tube furnace and an Anglicon temperature controller provided with a Chromel-Alumel thermocouple. The organic compound was first melted and soaked for half an hour at the melting temperature, before the temperature was raised further. The temperature was increased manually at a rate of $10^{\circ}/5$ min. The carbonization was carried out at 400° and 550° . At 400° carbonization, the holding time at 400° was 2 hours preceded by 0.5 hr soaking at 200° and 300° . At 550° carbonization, the holding time was 4 hours preceded by 0.5 hours soaking at 200° , 300° , 400° and 500° . The cokes were cooled under nitrogen before being exposed to the atmosphere. The cooled cokes were then ground in a pestle and mortar passed through a 40 mesh screen and extracted several times by stirring first with chloroform and then with benzene. Cokes which were gummy, especially those obtained at 400° were solvent extracted without being ground. The extracted cokes were dried first in the open atmosphere and then in a vacuum oven at 100° for about 6 hr. The dried cokes were then extracted with water in a Soxhlet apparatus to remove the aluminium chloride. The extraction was continued for two weeks, eventhough after one week no detectable chloride content was found in the extracting water as tested with AgNO_3 . The extracted cokes were dried first in the open atmosphere and then in a vacuum oven at 100° for about 24 hr. The cokes were cooled under vacuum and weighed. The yield were calculated as

$$\text{Yield}_1 (\%) = \frac{\text{Wt. of the residue (water extracted)}}{\text{Wt. of the aromatic compound}} \times 100$$

$$\text{Yield}_2 (\%) = \frac{\text{Wt. of the residue (before extraction with water-Introduced } \text{AlCl}_3)}{\text{Wt. of the aromatic compound}} \times 100$$

Ref: [6]

Degassing of Cokes: The same procedure was used for degassing of cokes as used in the earlier studies for animal charcoal [7] and carbon black 'Spheron 9' [8].

Reaction of the Cokes with the Base Solution: A procedure similar to that described earlier [7,8] was adopted.

RESULTS AND DISCUSSION

The benzene insoluble yields (B 1 %) of the cokes obtained from various aromatic compounds are given in Table 1. The yields of the cokes carbonized at 400° were not determined, because the cokes were so uncarbonized that even after ten times stirring (7 hr each time) with chloroform and benzene, the colour of the chloroform and benzene solution were dark brown in colour each time. This indicated that the coke structure had not fully developed at 400° carbonization temperature. The yields of the cokes

obtained from organic compounds, carbonized at 550° were in the following order naphthalene > 1-naphthol > 1-naphthoic acid > 1,8-naphthalic anhydride. This showed that compounds having lower melting points and molecular weight had carbonized to a greater extent. The lower yields of cokes obtained from 1-naphthol, 1-naphthoic acid and 1,8-naphthalic anhydride compared to that obtained from naphthalene might be due to the resistance offered by the functional groups in these cases to the formation of coke structure.

The yields of cokes determined on the two basis as described in the experimental section were quite different. The yields₁ were high compared to yields₂, which showed that aluminium chloride had not remained in the cokes in the same quantity as it was introduced, but most of it sublimed or decomposed during carbonization. Subtraction of the introduced aluminium chloride from the residues had greatly reduced the yields (yields₂).

The yields of the cokes also depended on the quantities of aromatic compounds being carbonized. The larger the amount of compound taken for carbonization, the lower was the yield. The amount of the compound taken for carbonization has been given in parenthesis in Table 1 with their respective yields of cokes. These differences in the yields might be due to frothing of the carbonizing material (when larger quantities of the compounds were taken) to the upper part of the pyrex tube during carbonization, which led to nonuniform and incomplete carbonization and so lower yields. When small amounts of the compounds were carbonized, the carbonizing material remained within

Table 1. Carbonization yields of various aromatic compounds.

Aromatic compound	Carbonization temp. 400°C Yield (%)	Carbonization temp. 550°C	
		Yield ₁ (%)	Yield ₂ (%)
Naphthalene	—	60(40) 75(10)	52(40) 66(10)
1-Naphthoic acid	—	36(10) 25(24) 30(10)	29(10) 15(24) 23(10)
1-Naphthol	—	37(40) 44(10)	29(40) 40(10)
1,8-Naphthalic anhydride	—	22(15) 30(10)	16(15) 25(10)

The number in the parentheses refer to the amount of the aromatic compound taken for carbonization.

a narrow temperature range. The carbonization was more uniform and complete and so higher yields were obtained.

Table 2 shows the uptakes of aqueous sodium hydroxide and alcoholic potassium hydroxide and cokes obtained by carbonizing various aromatic compounds at 550°. The uptake of aqueous sodium hydroxide by the naphthalene coke (not extracted with water) was considerably higher than the uptake of alcoholic potassium hydroxide by the same coke. This showed that the quite higher acidity in the aqueous medium might be due to the higher solubility of the acidic aluminium salt content of the coke in the aqueous medium compared to that in alcoholic medium. The uptake of aqueous sodium hydroxide by the naphthalene coke (extracted with water for 2 weeks) was lower than that of alcoholic potassium hydroxide. This showed that the acidity of the coke (water extracted) was not due to the presence of aluminium chloride, but because of some acidic groups on the surface of coke. This was confirmed by the finding that the acidity of coke (water extracted) shaken with deionized water for 72 hr at 30° was zero (Table 2 column 3). Any aluminium chloride present in the coke would have been extracted with water.

The uptake of aqueous sodium hydroxide by the naphthoic acid coke (water extracted) was about one half of the uptake of alcoholic potassium hydroxide by the same coke. In the case of naphthol coke (water extracted), the uptakes of aqueous sodium hydroxide and alcoholic potassium hydroxide were unexpectedly zero. The base uptakes of naphthalic anhydride coke (water extracted) were higher both in the aqueous and nonaqueous media compared to the base uptakes of cokes obtained from other compounds. In this case also the uptakes of alcoholic potassium hydroxide was higher than the uptake of aqueous sodium hydroxide.

These findings can be explained by proposing that the acidity of the water extracted cokes might be due to the presence of some acidic groups on the surface of cokes. The acidity of the water extracted naphthalene coke might be because of the formation of acidic surface complexes by reaction of the coke with the oxygen in the nitrogen gas, used during carbonization, or more likely due to reaction with atmospheric oxygen on exposure. Reaction of the cokes surface with water during their long extraction period could also have led to oxygenation.

The difference in acidity of the naphthoic acid and naphthalic anhydride cokes in the aqueous and alcoholic media shows that the nature of the surface groups on these cokes might have quite different characteristics from the functional groups of the original compounds. Functional groups like carboxyl and acid anhydride, if were present along on the surface of cokes would have been neutralized to a substantially equal extent in the aqueous and alcoholic media.

Table 2. Uptake of aqueous NaOH and alcoholic KOH by various cokes. Degassing temp. = 100°. React. temp. = 30°. React. time = 72 hr.

Coke samples	Uptake of aq. NaOH $\mu\text{equiv g}^{-1}$	Uptake of alcoh. KOH $\mu\text{equiv g}^{-1}$	Acidity of coke shaken with water $\mu\text{equiv g}^{-1}$
Naphthalene coke (unextracted with water)	1440	830	—
Naphthalene coke (extracted with water)	180	220	0
1-Naphthoic acid coke (extracted with water)	140	270	0
1-Naphthol coke (extracted with water)	0	0	0
1,8-Naphthalic anhydride coke (extracted with water)	230	340	0

In accordance to our earlier findings with charcoal [7] and 'Spheron 9' [8], this difference in the acidity of cokes in the aqueous and alcoholic media can be explained by proposing a keto-enol structure on the surface of these cokes.

The zero acid values of the naphthol coke both in the aqueous and alcoholic media were quite unexpected. Phenolic hydroxyl group, which is more stable at high temperature compared to carboxyl and other CO_2 -evolving groups, should have been present in considerable amount in the coke. It might be possible that phenolic hydroxyl groups have changed to some nonacidic oxygen groups such as ether groups during carbonization.

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