

## Acidic Functional Groups on the Surface of Animal Charcoal

M. ARSALA KHAN\* AND W. KEMP\*\*

\*Chemistry Department, Peshawar University, Peshawar, Pakistan.

\*\*Chemistry Department, Heriot-Watt University, Edinburgh, U.K.

(Received 27th March, 1982).

**Summary:** The surface acidity of the technical grade animal charcoal degassed at various temperatures was determined with bases of different strengths. The acidity on the surface of charcoal could be attributed to atleast two surface functional groups. The one which showed maximum decomposition at 300°C, might be a CO<sub>2</sub> evolving group. The other which still remained and appreciable amounts even when the charcoal was degassed at 700°C, might be some Co evolving group.

### Introduction

Surface acidity of charcoal, coal and carbon black has been a field of quite interest for the past few years. After realization by Shilov et al<sup>1,2</sup> that acid base character of carbon is due to surface oxygen complexes of definite structures, extensive study has been made to know the nature of these complexes on the surface of various types of charcoals, coals and carbon blacks. Of the surface complexes the acidic ones have been studied extensively compared to those with basic character. Even though many groups have been proposed to exist on the surface of carbon, the most acceptable ones are carboxyl, phenolic hydroxyl, lactones and quinone type carbonyl groups. These have been critically discussed in the review papers by Boehm<sup>3</sup>, Donnet<sup>4</sup>, Deviney<sup>5</sup>, Puri<sup>6</sup>, and Rivin<sup>7</sup>.

Barton et al<sup>8,9</sup> studied the neutralization behaviour of graphite and carbon black 'Sapheron 6' with aqueous sodium hydroxide and alcoholic sodium ethoxide as the samples were degassed at various temperatures. They observed that the uptake of sodium ethoxide was twice the value of sodium hydroxide for 'Spheron 6'. To explain their results of base uptakes and the one with Grignard reagent<sup>10</sup> they proposed the existence of n-lactone and f-lactone on the surface of 'Spheron 6', and f-lactone on the surface of graphite. Bansal et al<sup>11</sup> studied the neutralization behaviour of polymer carbons and postulated the existence of f-lactone on the surfaces of PVDC, PVC, PF, UF and Saran charcoals. They also observed higher uptake of sodium ethoxide compared to that of sodium hydroxide. They thought that low molarity of base solutions and insufficient time of equi-

libration were responsible for the low values of sodium hydroxide in the case of Barton et al<sup>8</sup>.

The present study was undertaken with a view to investigate whether potassium-tert-butoxide a stronger base than sodium ethoxide, neutralizes the acidic groups on the surface of charcoal to the same extent, or whether there are some weaker acidic groups as well which are neutralized to a greater extent by the stronger base potassium-tert-butoxide.

### Experimental

#### Degassing of Charcoal

A technical grade animal charcoal obtained from BDH, cleaned by extracting with benzene and dried at 100°C was used in this study. A procedure similar to Barton and Harrison<sup>12</sup> was used for degassing of charcoal. Degassing was done in a quartz tube 35 cm long and 2 cm in diameter. The tube had a side arm 8 cm long and ended in a B 14 cone for attachment to the vacuum line. A glass sinter was introduced across this arm to prevent any carbon particles going into the vacuum line. The main tube also ended in a B 14 cone to which could be attached three thin walled small pyrex bulbs through a three armed adapter. Degassing was done in a resistance tube furnace. The temperature was measured and controlled with Anglicon temperature controller using chromel Alumel thermocouple. The time of degassing was maintained 48 hours through out these experiments. After degassing the quartz tube was rotated to a slightly more than horizontal position and

\*To whom all correspondence should be addressed.

the carbon was tapped in the three bulbs in approximately equal amounts, which were then sealed off. The carbon in the bulbs were determined by weighing the bulbs along with other parts before and after sealing.

### Base Solution Preparation

Sodium-ethoxide and potassium-tert-butoxide solutions were prepared by refluxing freshly cut cleaned pieces of sodium and potassium in dried ethanol and tert-butanol respectively. The sodium ethoxide solution was diluted with ethanol only, however the potassium tert-butoxide solution was diluted with tert-butanol and dried benzene so that the final solution contained 20% benzene. Benzene was added to avoid freezing and to allow easy settling of charcoal. Sodium hydroxide solution was prepared in the usual way.

### Reaction of Carbon with Base Solutions

The thin walled glass bulbs containing the degassed charcoal were broken under nitrogen with a steel rod in conical flasks, each containing 25 ml of base solution. The flasks were then stoppered while under nitrogen, sealed with parafilm and was shaken for different duration of times using a thermostatted shaker. The temperature was maintained at  $34 \pm 1^\circ\text{C}$ . The suspensions were transferred to centrifuge tubes under nitrogen and centrifuged for about half an hour. Blank determination were made side by side similarly.

### Titration

Five mls of the clear supernant liquid from each centrifuge tube was transferred to a titration flask, to which 25 mls of deionized water had been added in the case of sodium ethoxide and 25 ml of neutralized methylated spirit in the case of potassium tert-butoxide. The solutions were titrated with standard HCl solution using bromothymol blue as indicator.

### Results and Discussion

The uptake of sodium ethoxide and potassium-tert-butoxide by charcoal degassed at various temperatures is shown in Fig I. It can be noticed that the

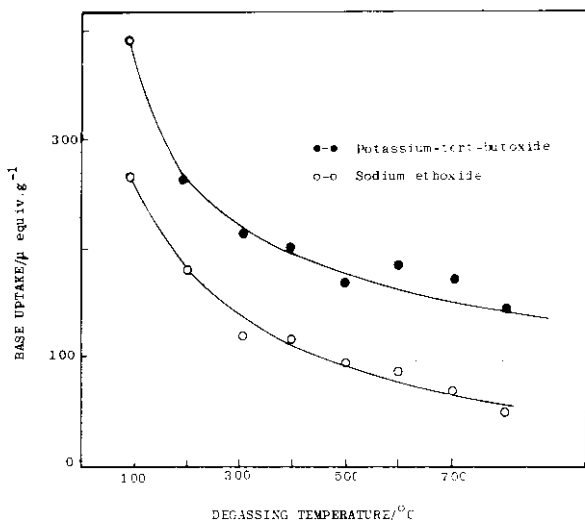


Fig. 1. Effect of Degassing Temperature on the Base Uptake of Animal Charcoal.

decrease in the base uptakes with increase in the degassing temperature is quite appreciable in the 100-300 $^\circ\text{C}$  temperature range, whereas a small gradual decrease in the base uptakes can be seen in the temperature range 300-800 $^\circ\text{C}$ . Moreover it can be seen that even by degassing the charcoal at 800 $^\circ\text{C}$ , both the bases showed some uptakes, which is quite appreciable in the case of potassium tert-butoxide. This shows that there may be at least two type of functional groups on the surface of charcoal. The one which decomposes mostly in the 100-300 $^\circ\text{C}$  temperature range may be neutralized equally by both the bases because both the bases show an equal drop of their uptakes in this range. The other functional group which remains in appreciable quantity even by degassing the charcoal at 800 $^\circ\text{C}$  may also be neutralized by both the bases, however the neutralization with sodium ethoxide does not take place to an appreciable extent within 2 hours. More experiments under different experimental conditions were performed using sodium hydroxide, sodium ethoxide and potassium tert-butoxide. The results of these experiments are given in table 1. Column 1 shows the uptake of these bases, when the molarities of the base solutions were 0.05M, time of reaction was 2 hours and the degassing temperature of

Table 1. Uptake of Various Bases Under Different Experimental Conditions by Charcoal ( $\mu\text{equiv g}^{-1}$ )

Expt. conditions	React. time = 2 hr Base sol. = 0.05M Degassing temp. = 100°C	React. time = 2 hr Base sol. = 0.2M Degassin temp = 100°C	React time = 72 hr Base sol. = 0.2M Degassing temp = 100°C	React. time = 72 hr Base sol. = 0.2M Degassing temp. = 700°C
Aq. sodium hydroxide	76	117	189	20
Sodium ethoxide in ethanol	263	296	580	270
Potassium tert-butoxide in 80% tert-butanol and 20% benzne	389	400	792	342

charcoal was 100°C. It is evident that the neutralization capacity of these bases are in the order of potassium tert-butoxide > sodium ethoxide > sodium hydroxide. The neutralization capacity of sodium ethoxide is higher than sodium hydroxide (more than thrice the value of sodium hydroxide). The uptake of potassium tert-butoxide is higher than that of sodium ethoxide. It was thought initially that these differences in the uptake of different bases might be due to low molarity and short period of reaction time as observed by Puri and Bansal<sup>13</sup>. In column 2 values of base uptakes are given when the molarity of base solutions was 0.2 M and the time of reaction was 2 hours. An increase in the uptake of these bases can be noticed. Column 3 shows the values when the reaction time was prolonged to 72 hours, whereas the molarity of the base solutions was kept 0.2 M. An appreciable increase in the uptake of these bases can be observed. Moreover the uptake of aqueous sodium hydroxide is considerably lower compared to that of sodium ethoxide and potassium tert-butoxide.

These findings give further support to the view that there are at least two type of functional groups on the surface of charcoal. The one may be neutralized completely by all the three bases under prolonged reaction time and concentrated base solutions, whereas the other may be so weak that it cannot be neutralized with aqueous sodium hydroxide but is neutralizable with stronger bases sodium ethoxide and potassium tert-butoxide to different extents.

Column 4 shows the uptake of bases by charcoal degassed at 700°C. The time of reaction and the molarity of the base solutions were maintained 72 hours and 0.2M respectively. The acidity found with sodium hydroxide nearly deminished to zero at 700°C degassing temperature, which is in agreement with the results of previous workers<sup>6,8,9,11</sup>. However the acidity found with sodium ethoxide and potassium tert-butoxide are appreciably higher. This indicates that the functional group which is neutralized with sodium ethoxide and potassium tert-butoxide but not with sodium hydroxide is quite stable and remains to an appreciable extent even at 700°C. However the group which is neutralized with sodium hydroxide as well is diminished completely by degassing the charcoal at 700°C.

From the literature it is evident that the uptake of sodium hydroxide has a stoichiometric relationship with the evolved CO<sub>2</sub> and that the evolution of CO<sub>2</sub> drops to a negligible value in the 700-800°C temperature range<sup>13-16</sup>. By analogy it can be said that in the case of our charcoal sample also, it may be the CO<sub>2</sub> evolving group or groups which are neutralized with sodium hydroxide. Sodium ethoxide and potassium tert-butoxide may be neutralizing some other groups, in addition to those which are evolved as CO<sub>2</sub>. Puri<sup>6</sup> found that the evolution of CO from the surface of charcoal started in the 500-700°C temperature range and was nearly completely removed at 1000°C. Again by analogy we can say that the acidity found with sodium ethoxide and potassium tert-butoxide but not with sodium hydroxide

may be due to CO evolving groups, because even though there is considerable uptake of these stronger bases at 700°C degassing temperature, a noticeable drop in acidity occurs at 700°C. This is the temperature at which CO also shows maximum evolution.<sup>6</sup>

From our results we can conclude that at least two types of functional groups may be responsible for the acidity of charcoal. The one which is neutralized with sodium hydroxide and the stronger bases may be a CO<sub>2</sub> evolving group, whereas the other which is neutralized with sodium ethoxide and potassium tert-butoxide but not with sodium hydroxide may be a CO evolving group. Effect of high porosity and ash content of charcoal on the uptakes of various bases cannot be ignored.

### Acknowledgement

The authors are grateful to Prof. B. G. Gowenlock and Professor J. G. Buchanan for providing research facilities and the Government of Pakistan for providing financial support.

### References

1. N. Shilov, H. Shatonovskaya and K. Chmutov, *Z. Physik. Chem.*, A **149**, 211 (1930).
2. N. Shilov, *Kolloid Z.*, **52**, 107 (1930).
3. H.P. Boehm, *Advan. Catalysis*, **16**, 179 (1966).
4. J. B. Donnet, *Carbon*, **6**, 161 (1968).
5. M. L. Deviney, Jr, *Advan. Colloid and Interface Science*, **2**, 237 (1969).
6. B. R. Puri in P. L. Walker Jr, *Chemistry & Physics of Carbon*, (Marcel Dekker, New York, 1970) vol. 6, p. 191.
7. D. Rivin, *Rubb. Chem. Technol.*, **44**, 307 (1971).
8. S. S. Bartoń, D. Gillespie & B. H. Harrison, *Carbon*, **11**, 649 (1973).
9. S. S. Barton, G. L. Boulton & B. H. Harrison, *Carbon*, **10**, 295 (1972).
10. S. S. Barton & B. H. Harrison, *Carbon*, **13**, 283 (1975).
11. R. C. Bansal, N. Bhatia & T. L. Dhami, *Carbon*, **16**, 65, (1978).
12. S. S. Barton & B. H. Harrison, *Carbon*, **10**, 245, (1972).
13. B. R. Puri & R. C. Bansal, *Carbon*, **1**, 451, 457, (1964).
14. B. R. Puri, Y. P. Myer & L. R. Sharma, *Res. Bull. Punjab Univ. India*, **88**, 53, (1956).
15. B. R. Puri, Y. P. Myer & L. R. Sharma, *J. Indian Chem. Soc.*, **33**, 781 (1956).
16. B. R. Puri, Y. P. Myer & L.R. Sharma, *Chem. & Ind (London)* R. 30, (1956).