

## A Keto-enol Interpretation of the Surface Acidity of Carbon Black 'Spheron 9'

M. ARSALA KHAN<sup>\*a</sup> AND W. KEMP<sup>b</sup>

<sup>a</sup>Chemistry Department, Peshawar University, Pakistan.

<sup>b</sup>Chemistry Department, Heriot-Watt University, Edinburgh, U.K.

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**Summary:** Surface acidity of carbon black 'Spheron 9' has been studied using bases of different strengths. Three type of acidic groups have been proposed to exist on the surface of 'Spheron 9'. The one which showed maximum decomposition in the 100-300°C temperature range and which was neutralized with sodium bicarbonate only was thought to be either physically adsorbed CO<sub>2</sub> or some strongly acidic CO<sub>2</sub> evolving group such as carboxyl group. The other group which was totally eliminated at about 700°C and which was neutralized with aqueous sodium hydroxide and the stronger bases, but not with sodium bicarbonate was suggested to be a weakly acidic CO<sub>2</sub> evolving f-lactonic group. The third group which remained in appreciable quantity even by degassing the carbon at 700°C and which was neutralized with the stronger bases and with alcoholic potassium hydroxide and sodium hydroxide but not with aqueous sodium hydroxide and sodium bicarbonate was thought to be a weakly acidic CO evolving keto-enol group. The keto-enol group has been found to be the major group on the surface of 'Spheron 9'

### Introduction

Studies on the nature of acidic functional groups on the surfaces of charcoals and carbon blacks have been performed by previous workers using different techniques and have been thoroughly discussed in review papers<sup>1,2,3,4,5</sup>. Work of Barton et al<sup>6,7</sup> on graphite and carbon balck 'Spheron 6' and Bansal et al<sup>8</sup> on PVDC, PVC, PF, UF and Saran Charcoals using aqueous sodium hydroxide and alcoholic sodium ethoxide, indicated the existence of surface lactonic groups. Study on animal charcoal using sodium hydroxide, sodium ethoxide and potassium tert-butoxide has been earlier performed by Khan and Kemp<sup>9</sup>. They found a great difference in the uptakes of these bases which was explained by proposing the existence of at least two acidic functional groups on the surface of charcoal. They thought that high porosity and high ash content of charcoal might have also effected the uptakes of these bases.

The earlier study on charcoal was continued with carbon balck 'Spheron 9' with the view to establish, whether the differences in the uptake of the various bases in the case of charcoal<sup>9</sup> was due actually to different surface functional groups or high porosity and high ash content of charcoal have led to these differences. Carbon black 'Spheron 9' is a nonporous material and has also a negligible ash content.

### Experimental

Carbon black 'Spheron 9' obtained from Cabot Corporation was used in this study. The carbon black was cleaned by extracting with benzene in a Soxhlet apparatus and was dired at 100°C. The carbon black was degassed at various temperature upto a vacuum of 10<sup>-6</sup> mm Hg. The procedures for degassing of carbon, preparation of base solutions and reaction of carbon with the base solutions were similar to that described earlier<sup>9</sup>.

### Results and Discussion

The loss in weight of carbon black 'Spheron 9' degassed at various temperature is shown in Fig-I. A considerable loss in weight can be noticed in the 200-300°C, 400-500°C and 600-700°C temperature ranges. This indicated the presence of at least three types of functional groups which have different stabilities and have their maximum decomposition in the 200-300°C, 400-500°C and 600-700°C temperature ranges.

Fig-II shows the uptakes of 0.05M sodium ethoxide potassium isopropoxide and potassium tert-butoxide by carbon at different reaction times. All the bases showed a small increase in their uptakes with increase in the reaction time.

\*To whom all correspondence should be addressed.

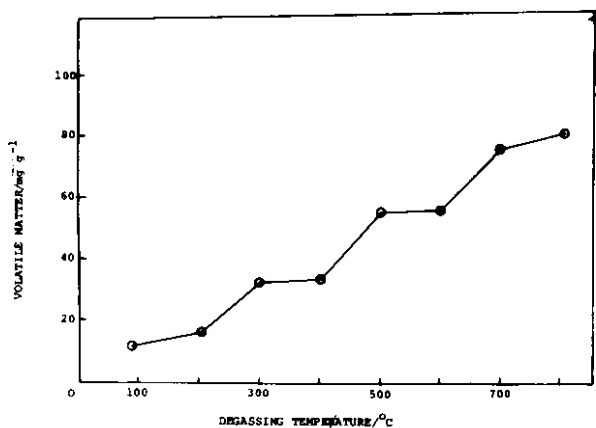


Fig. 1. Loss in Weight of 'Spheron 9' at Various Degassing Temperatures.

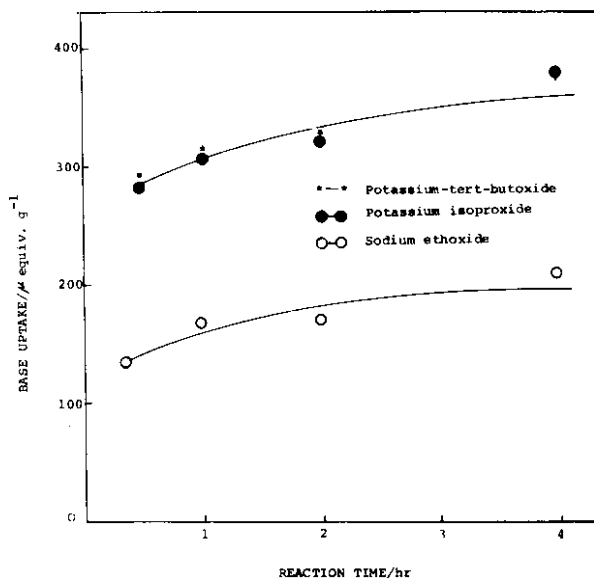


Fig. 2. Uptake at Various Reaction Time by 'Spheron 9'

The uptakes of 0.05M sodium ethoxide, potassium isopropoxide and potassium-tert-butoxide by carbon degassed at various temperatures is shown in Fig-III. The time of reaction was kept 2 hours like Barton et al<sup>6,7</sup> and Khan and Kemp<sup>9</sup>. A considerable difference in the uptakes of these bases is apparent. All of these bases showed a small decrease in their uptakes upto 300°C and a more rapid decrease onward, which dropped to a negligible value at 800°C degassing temperature. Earlier workers<sup>6-8,10-12</sup> also observed that the acidity of carbon diminished nearly completely at about 700-800°C degassing temperature. They correlated the acidity of

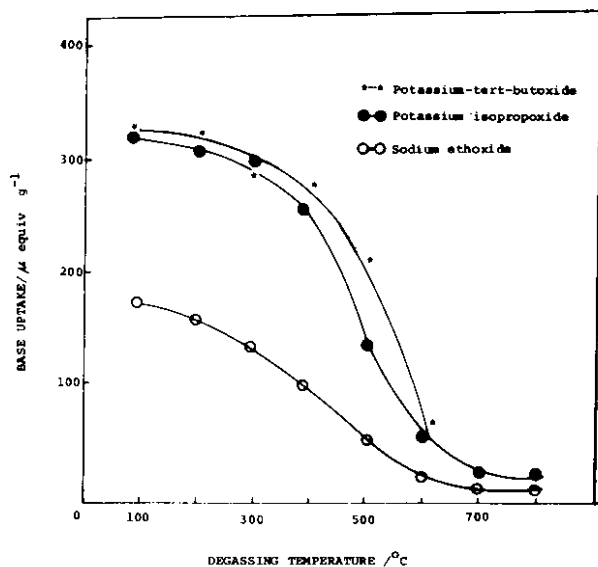


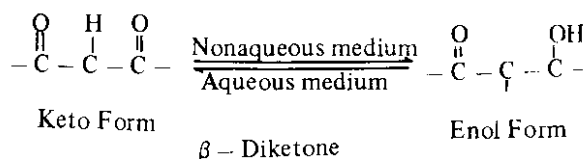
Fig. 3. Effect of Degassing Temperature on the Base Uptake of 'Spheron 9'.

carbon to acidic surface groups which evolve as CO<sub>2</sub> on degassing, because the temperature at which the acidity of carbon diminished completely, CO<sub>2</sub> also showed complete elimination. Moreover they also found that the evolved CO<sub>2</sub> had stoichiometric relationship with the decrease in the base uptake. They did not find any relationship between the base uptakes and the evolved CO. They also observed that even though CO showed maximum evolution in the 500-700°C temperature range, it still remained in appreciable quantity even when the carbon was degassed at 800°C. It was thought initially that the acidity of 'Spheron 9' in our case might be due to the presence of two CO<sub>2</sub> evolving surface groups, decomposing in the 100-300°C and 300-800°C temperature ranges respectively. The quite low uptake of sodium ethoxide compared to that of potassium isopropoxide and potassium tert-butoxide was thought to be due to low molarity (0.05 M) of base solution, and short period of reaction time (2 hours), where reaction with sodium ethoxide a comparatively weaker base, did not reach to the same extent as that with the stronger bases. However later results (Table 1) pointed the existence of a third acidic group, which remained in appreciable quantity even when the carbon was degassed at 700°C (Table-I, column 4). This surface group was so weak that complete neutralization did not occur with 0.05M base solutions with in 2 hours reaction time (Table I, column 1). A considerable increase in the uptakes of various bases

was found by increasing the concentration of the base solutions to 0.2 M and the time of reaction to 72 hrs (Table I, column 2 & 3). It can also be noticed that the acidity measured with aqueous sodium hydroxide of carbon degassed at 700°C has nearly completely diminished even when the carbon was reacted with the base solution for 72 hours, whereas the acidity measured with the stronger bases was quite high (Table I, column 4). The surface groups which have been neutralized with aqueous sodium hydroxide and which have been completely eliminated at 700°C might be some CO<sub>2</sub> evolving acidic groups. Previous workers<sup>8</sup> have also attributed the acidity measured with aqueous sodium hydroxide to the CO<sub>2</sub> evolving lactonic groups. The acidity measured with the stronger bases and not with aqueous sodium hydroxide might be due to some CO evolving surface groups. Surface groups which evolve as CO have been reported to remain in considerable quantity even when the carbon was degassed at 700°C<sup>6-8,10-12</sup>.

It is interesting to point out that the acidity of carbon measured with alcoholic potassium hydroxide

and sodium hydroxide was considerable even higher than that of potassium isopropoxide and potassium tert-butoxide. (Table I, column 3). This can be explained by suggesting that the group which was neutralized with the stronger bases and with alcoholic potassium hydroxide and sodium hydroxide but not with aqueous sodium hydroxide might have a keto-enol structure. In keto-enol system such as β-diketones, the equilibrium shifts to the nonacidic keto form in aqueous medium and to the acidic enolic form in nonaqueous medium as<sup>13-15</sup>:



The results of this study can be explained by suggesting the presence of carboxyl, *l*-lactone and keto-enol groups on the surface of 'Spheron 9'. The carboxyl content was determined with sodium bicarbonate (Table I, column 3). Sodium bicarbonate has

Table 1. Uptake of Various Bases Under Different Experimental Conditions by 'Spheron 9' (μequiv g<sup>-1</sup>)

| Expt. Condition<br>Bases                                    | React time = 2 hr<br>Base sol. = 0.05 M<br>Degassing temp.<br>= 100°C | React time = 2 hr<br>Base sol. = 0.2 M<br>Degassing temp.<br>= 100°C | React time = 72 hr<br>Base sol. = 0.2 M<br>Degassing temp.<br>= 100°C | React time = 72 hr<br>Base sol. = 0.2 M<br>Degassing temp.<br>= 700°C |
|---|---|--|---|---|
|   | Aq. sodium bicarbonate  | —  | —   | 39  |
| Aq. sodium hydroxide  | 116   | 150  | 197   | 10  |
| Alcoh. sodium hydroxide                                     | —   | —  | 888   | —   |
| Aq. potassium hydroxide                                     | —   | —  | 210   | —   |
| Alcoh. potassium hydroxide                                  | —   | —  | 840   | —   |
| Alcoh. sodium ethoxide                                      | 170   | 214  | 679   | 121   |
| Potassium isopropoxide in isopropanol                       | 323   | —  | 711   | 232   |
| Potassium tert-butoxide in 80% tert-butanol and 20% benzene | 323   | 331  | 851   | —   |

Table II. Amount of Different Acidic Groups on the Surface of 'Spheron 9'  
( $\mu\text{equiv. g}^{-1}$ )

| Carboxyl group              | f-Lactone Group  | Keto-Enol Group   |
|-----------------------------|--|---|
| 39 (Aq. Sodium bicarbonate) | 158<br>(Aq. Sodium hydroxide-<br>Aq. sodium bicarbonate) | 691 (Alcoh. Sodium hydroxide-<br>Aq. Sodium hydroxide)<br>6 43 Alcoh Potassium hydroxide-<br>-Aq. Sodium hydroxide).<br><br>482 (Sodium ethoxide- Aq. So-<br>dium hydroxide).<br><br>512 (Potassium isopropoxide-<br>Aq. Sodium hydroxide).<br><br>652 (Potassium-tert- butoxide-<br>Aq. Sodium hydroxide). |

been reported to neutralize completely the strongly acidic carboxyl groups only<sup>1</sup>. The content of f-lactonic group was found by subtracting the acidity measured with sodium bicarbonate from that measured with aqueous sodium hydroxide. The amount of keto-enol surface group was obtained by subtracting the acidity measured with aqueous sodium hydroxide from that measured with the stronger bases or alcoholic sodium hydroxide and potassium hydroxide. The results are given in Table II. The reactions of these acidic groups with various bases under different reaction conditions are shown above.

The R group was assumed to be some bridging group such as ether linkages between two graphitic platelets of the carbon microcrystallites.

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