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Acid-base properties of carbon black surfaces

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ACID-BASE PROPERTIES OF CARBON BLACK SURFACES

By
Roy Eugene Test
Robert S. Hansen

May 1961

Ames Laboratory
Iowa State University
Ames, Iowa
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ACID-BASE PROPERTIES OF CARBON BLACK SURFACES*
by
Roy Eugene Test and Robert S. Hansen

ABSTRACT

The surface properties of carbon blacks reflect not only Van der Waals forces due to carbon, but also chemical properties of groups formed on carbon black surfaces by reactions with environmental substances (e.g. water, oxygen, etc.). The present work constitutes a study of such groups.

Carbon black is known to be graphitic in character, with carbon atoms occurring in sheets; their arrangement is essentially that of the polynuclear aromatic compounds. An idealized carbon black, one which consists of nothing but carbon, must then either display free radicals at all carbons occurring on sheet edges, or else must markedly distort its structure along the edges in an effort to eliminate such radicals. It is not surprising, therefore, that a pure carbon black is almost impossible to obtain, and that a carbon black surface appears to be covered with such functional groups as might be expected to result from the reaction of free radicals or highly strained unsaturated structures with gases to which it has been exposed. These groups might be expected to react in manners similar to the reactions of comparable organic chemicals. However these groups might be expected to behave differently, in some respects, from similar groups which are attached to small simple molecules.

*This report is based on an M.S. thesis by Roy Eugene Test submitted May, 1961, to Iowa State University, Ames Iowa. This work was done under contract with the Atomic Energy Commission.
A certain portion of the oxygen chemically adsorbed by carbon black was found to behave in a manner closely similar to the behavior of organic carboxylic acids; desorption as carbon dioxide occurred at temperatures and conditions of decarboxylations, diazomethane uptake paralleled closely esterification of carboxylic acids. However it appeared that lithium aluminum hydride was not able to reduce these carboxyl groups to alcohols. These conclusions confirm and extend the conclusions of Studebaker et al. (2).

Treatment of carbon black with hydrogen peroxide was found to markedly increase the amount of chemisorbed oxygen desorbable as carbon dioxide without increasing the active hydrogen content of the carbon black. This indicated that groups were present on the surface which would be oxidized by hydrogen peroxide. The oxidation products released carbon dioxide upon pyrolysis.

Carbon blacks were analyzed for active hydrogen by lithium aluminum hydride treatment; significant reductions resulted from thermal decarboxylation and esterification treatments; other treatments did not cause significant variations in active hydrogen, although small variations might have been masked by the reaction of small amounts of water adsorbed by the carbon.

Adsorption of base by carbon black at various concentrations of supporting electrolyte was studied as a function of
pH and time. It was found that the rate of adsorption of base on carbon black depends strongly on stirring rate. This suggests that the rate of the reaction is diffusion controlled. Quantity of base adsorbed was found to vary linearly with pH over an extensive pH range. This suggested an analysis of the titration curves by electrical double layer theory; the double layer capacity calculated from the titration curves was found to be fairly close to that found at mercury-electrolytic solution and silver iodide-electrolytic solution interfaces. However, exact agreement was not found to exist between the actual capacity change with change in ionic strength and that predicted by diffuse double layer theory.
INTRODUCTION

The structure of carbon blacks is comparable to the structure of graphite. The carbon atoms in graphite are arranged in planes. Each plane is made up of a two dimensional hexagonal net of carbon atoms in which the bond distance between nearest atoms is 1.42 Å. These planes are stacked one on top of another in such a way that half of the atoms in a layer is directly over atoms in the previous layer and the other half is over the centers of the hexagons. The third layer is over the first layer. The distance between the layers is 3.35 Å. Figure 1 shows a small part of one of these planes. Figure 2 shows the edge of a crystal plane of a very pure carbon black.

The carbon black structure also has planes of carbon atoms like those in graphite; however, the planes in carbon black are not arranged in a regular pattern as in graphite, but are rotated with respect to one another in a more or less random manner. In addition, the carbon black particles are extremely small, the specific surface areas of carbon blacks are hence large, and surface properties very important. Because the particles of carbon black are so small, there are many carbon atoms situated at the edges of crystal planes. These atoms cannot be bound to three other carbon atoms as is the case of atoms in the interior of the crystal. Figure 3
Figure 1. Arrangement of carbon atoms in the graphite lattice

Figure 2. Edge of a crystal plane of a very pure carbon black
Figure 3. Proposed model of the edge of a crystal plane in an actual carbon black lattice
gives a simplified model of how an edge would look if the carbon black were very pure. The indicated free radicals are not expected to be stable in the presence of atmospheric oxygen, water vapor and the like unless the carbon has some way to stabilize these radicals. Therefore, it is not surprising that the surface groups of types shown in Figure 3 are present on the carbon blacks.

The surface groups shown in Figure 3 have been postulated by various workers to explain their experimental data. Kruyt and de Kadt (1) proposed that carboxyl groups were present on carbon black surfaces. Studebaker et al. (2) proposed that 1,4-quinone groups were present as well as carboxyl groups and phenols. Garten and Weiss (3) proposed that phenols and lactones were present, but carboxyl groups were absent from carbon black surfaces. The experimental evidence suggesting the existence of these groups will be given at the end of the next section.

Expected Chemical Behavior of Surface Groups

It is proposed that the surface groups on carbon black should behave in a manner that can be predicted from the behavior of similar groups in common organic molecules. Using this assumption, the expected behavior of these surface groups will include the following features:

1. Reactions of carboxyl groups: The unsubstituted
monobasic acids are quite stable to thermal decarboxylation. This is true for both aliphatic and aromatic acids. The temperature necessary to bring about this reaction is about the temperature necessary to carbonize the compound. This temperature is about 500 to 600°C for many compounds. The expected reaction is

\[
(1) \quad \text{RCOOH} \xrightarrow{\Delta} \text{RH} + \text{CO}_2
\]

Since there is no danger of destroying the carbon by heat, one may use as high a temperature as necessary.

Lithium aluminum hydride is a compound that is soluble in ether and reacts with carboxyl groups in the following way:

\[
(2) \quad 4\text{RCOOH} + 3\text{LiAlH}_4 \rightarrow \text{LiAl(OCH}_2\text{R})_4 + 2\text{LiAlO}_2 + 4\text{H}_2
\]

\[
4\text{H}^+ + \text{LiAl(OCH}_2\text{R})_4 \rightarrow \text{Li}^+ + \text{Al}^{+3} + 4\text{RCH}_2\text{OH}
\]

These reactions permit conversion of carboxyl groups to alcohols.

Diazomethane has been used to study carbon blacks with some degree of success. It is a good methylating reagent and will form methyl esters with carboxyl groups as follows:

\[
(3) \quad \text{RCOOH} + \text{CH}_2\text{N}_2 \rightarrow \text{RCOOCH}_3 + \text{N}_2
\]

Diazomethane is a very useful reagent for the study of carbon black surfaces because the only product formed besides the ester is a gas, nitrogen.

Grignard reagents have also been used successfully on
carbon blacks. Grignard reagents react with carboxyl groups according to the following equation:

\((4) \quad \text{RCOOH} + \text{CH}_3\text{MgI} \rightarrow \text{RCOOMgI} + \text{CH}_4\)

Note that reactions 1-4 form one mole of gaseous product per mole of carboxyl group. In principle, the above reactions furnish four independent methods for the determination of the number of carboxyl groups on the carbon surface. However, phenols undergo reactions with the above reagents to give the same gaseous products. This is indicated in the next section.

2. Reactions of phenolic groups: Lithium aluminum hydride and the Grignard reagent react with phenols as follows to release one mole of hydrogen and one mole of methane respectively per mole of phenol group.

\((1) \quad 4\text{ArOH} + \text{LiAlH}_4 \rightarrow \text{LiAl(OAr)}_4 + 4\text{H}_2\)

\((2) \quad \text{ArOH} + \text{CH}_3\text{MgI} \rightarrow \text{ArOMgI} + \text{CH}_4\)

With diazomethane phenols react to form ether groups releasing one mole of nitrogen per mole of ether group formed.

\((3) \quad \text{ArOH} + \text{CH}_2\text{N}_2 \rightarrow \text{ArOCH}_3 + N_2\)

Note that phenols form ethers with diazomethane and carboxyl groups form esters. These groups should behave differently on hydrolysis.

3. Carbonyl groups: Carbonyl groups react with lithium aluminum hydride and Grignard reagent without releasing any
gaseous products. Carbonyl groups react stoichiometrically with the reagents. Therefore the number of carbonyl groups present on the surface can be determined by measuring the amount of reagent used. The equations for the reactions are as follows:

(1) \[ 4R_2C=O + LiAlH_4 \rightarrow LiAl(OCHR_2)_4 \]
\[ LiAl(OCHR_2)_4 + 4H^+ \rightarrow Li^+ + Al^{+3} + 4R_2CHOH \]

(2) \[ R_2C=O + CH_3MgI \rightarrow R_2(CH_3)COMgI \]

Diazomethane can add across a double bond to form a pyrazoline ring. 1,4-quinones are not aromatic in character and the bonds in the ring act as if they were unsaturated double bonds. Reaction of a carbon black with diazomethane should give a carbon with an increased nitrogen content if 1,4-quinones are present.

The above reactions offer experimental methods for determination of the total amounts of each of the above functional groups on the carbon black surface. A measurement of the carbon dioxide formed by reaction 1-1 will give the number of carboxyl groups present. Measurement of the hydrogen released from reactions 1-2 and 2-1 will give the number of carboxyl groups plus the number of phenolic groups. The number of phenolic groups can be found by difference. By measuring the total amount of lithium aluminum hydride used the number of carbonyl groups can be found; this is equal to the amount of lithium aluminum hydride used minus the
amount used by the phenolic groups and the amount used by the carboxyl groups. The number of 1,4-quinones can be measured by measuring the nitrogen content of the carbon after reaction with diazomethane. Structures have been postulated for carbon blacks in which there was unsaturation other than that due to quinones. Therefore, the above procedure may not measure solely 1,4-quinones. Other methods have been proposed to measure the unsaturation on carbon such as catalytic hydrogenation and bromine addition.

All of the above experimental methods have been tried on carbon blacks with varying degrees of success either by the author or by other workers. Other experimental methods have also been tried such as infrared analysis (4), polarographic analysis (4), measurements of the products from high temperature evacuations (5), and analysis of the emission spectra of carbons while under bombardment with high speed electrons (6). The results obtained by these methods point to the existence of functional groups on carbon surfaces which are similar in character to carboxyl, phenolic, carbonyl and quinone groups found in common organic molecules.

4. Acid base properties of carbon blacks: The reaction of an acid with the hydroxide ion is usually represented as follows:

\[ \text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \]

The carboxyl group is usually a moderately weak acid and
phenolic groups are usually very weak acids. Since no evidence is available concerning the acidity of these groups on the carbon surface, it seems reasonable to assume that the carboxyl and phenolic groups will have about the same relative acidity as they do on most organic molecules. It should therefore prove possible to titrate carbon blacks with base potentiometrically. There are several reasons for expecting the titration curves to be far more complex than that of a mixture of acetic acid and phenol in water.

One reason that can be given for the complexity of the titration curve is that all of the carboxyl groups or phenolic groups may not be identical in acid strength. The acidity of carboxyl and phenolic groups in a benzene ring depends strongly on other substituents in the same ring. For example, benzoic acid has a pK of 4.6 whereas salicylic acid has a pK of 2.97 and 2,6, dihydroxybenzoic acid has a pK of 1.3. Similar examples can be cited for phenols. The compound phenol has a pK of 9.96 whereas o-nitrophenol has a pK of 2.17 and 2,4,6, tri-nitrophenol (picric acid) is considered to be a strong acid. The type of group, the number of groups and the position of the group have very large effects on the acidity of aromatic acids. Due to the structure of carbon black, the rings on which the acid groups are attached would not all be alike. This would give the acid groups a wide spectrum of acidities. A potentiometric titration of these
acid groups would give a curve in which there was no titrimetric end point.

Another reason, and probably more important one, has to do with charging of the surface of the carbon black due to the ionization of the acid groups. A negative charge already present makes the creation of another negative charge close by much more difficult. An example of this is given by oxalic acid. The first dissociation constant of oxalic acid is $6.5 \times 10^{-2}$ and the second dissociation constant is $6.1 \times 10^{-5}$. For this reason, the titration curve of carbon black would be expected to resemble those of polybasic acids in which the numbers of carboxyl groups is large. In this respect, carbon black should resemble proteins and cation exchange resins.

Before closing this introduction, the work already performed on the above reactions will be briefly reviewed. Prior to 1929, most published work on pure activated carbons was restricted to carbons activated at high temperatures and it was not known that an ash free carbon could adsorb alkali. In 1929, Kruyt and de Kadt (1) observed that sugar carbons activated in air at low temperatures adsorb alkali. It has later been shown that other carbons behave similarly. Maximum base adsorption was observed for carbons activated in the temperature range 400-500°C. This is also the temperature at which the greatest amount of oxygen can be fixed. Activation at temperatures above 500°C results in decreased base
adsorption; little or no base is adsorbed by carbons activated at temperatures above 800°C. Kruyt and de Kadt suggested that carboxyl groups were formed when the carbon was activated at the low temperature. The loss of the ability to adsorb alkali upon increase of activation temperature was thought to be due to decarboxylation of these groups.

Villars (7) made the first attempt to determine the behavior of the surface groups on carbon by chemical methods other than alkali adsorption. He treated carbon blacks with methyl magnesium iodide and measured the amount of methane evolved, and the total amount of reagent used. With the Grignard reagent, it is not possible to distinguish between carboxyl and phenolic groups since both groups react with the reagent to release methane. Villars assumed that the methane evolved was due to phenolic hydroxyl groups. By using this assumption he calculated the amount of oxygen attached to the active hydrogen. The reagent used without evolution of methane was thought to be due to its reaction with carbonyl groups. Villars was able to account for 26% of the total oxygen content of the carbon by this method; about 18% of the total amount was of the carbonyl type.

Studebaker et al. (2) used diazomethane as a reagent for the study of the surface groups on carbon. They found that this reagent produces two types of methoxy groups when carbon black is treated with it. One type can be hydrolyzed with
dilute acid, and the other type cannot be hydrolyzed. The type that can be hydrolyzed with dilute acid was thought to be a methyl ester of a carboxyl group and the other type was considered to be a methyl ether of phenolic hydroxyl groups. They also found that the nitrogen content of the carbon was increased by reaction with diazomethane. This nitrogen could not be removed by washing with water. This increase in nitrogen was thought to be the result of the formation of pyrazoline rings with 1,4-quinones. This proposal was tested by treating the carbon with sodium borohydride and measuring the amount of hydrogen taken up. Sodium borohydride reduces quinones to hydroquinones. They also tried catalytic hydrogenation of the carbon using Adams catalyst. There was a good correlation between amounts of hydrogen taken up by the sodium borohydride treatment and by catalytic hydrogenation. For every two atoms of hydrogen taken up by the carbon from the sodium borohydride, four atoms of hydrogen were taken up by the carbon from the catalytic hydrogenation. However, the amount of nitrogen was always less than that expected from the above results. This was explained by assuming that some of the nitrogen was removed by washing. The difference may very well have been due to steric hindrance which prevented the formation of the pyrazoline rings.

Garten and Weiss (3) looked at the titration curves of carbon blacks obtained by themselves and by Villars (8) and
concluded that carboxyl groups were absent from the surface of carbon. They compared the titration curves of several carbon blacks with those of resins which contained phenols and which contained carboxylic acids. The titration curves of the carbons were more similar to those of the phenol containing resins than those of the carboxyl containing resins. In actual fact, the carbon curves were in between those for the "ideal" substances.

To explain the findings of Studebaker et al. (2) that two methoxy groups were formed when diazomethane was added to carbon blacks, it was necessary to postulate the existence of still another group. Lactones of the type found in fluorescein and phenolphthalein can be methylated with diazomethane. The resulting ester can be hydrolyzed with dilute acid. The dissociation constant of phenolphthalein is $1.15 \times 10^{-9}$. This would explain the titration curve and also the existence of a group that forms hydrolyzable esters with diazomethane.

The number of carboxyl and phenolic groups found by Studebaker was always less than that which would have been necessary to explain amount of base adsorbed by the carbon. Studebaker thought that this was due to carboxyl and phenol groups which were too hindered to react with the diazomethane. Garten and Weiss (3) thought this unlikely and postulated another group to explain the deficiency. The normal lactones, i.e. lactones formed from the dehydration of hydroxy acids, do not form
esters when treated with diazomethane. They do react with base which results in opening of the ring. By postulating these groups, Garten and Weiss were able to explain qualitatively all phases of reaction of base with carbon black. However, they offer no evidence to support their theory except the titration curves.
OBJECTIVES OF THE PRESENT RESEARCH

The objectives of the present research were as follows:

1. To see whether reactions of carbon blacks with reagents such as lithium aluminum hydride, diazomethane, and base, and decarboxylation behavior, can be rationalized by a consistent model of the carbon surface. The reagents and reactions mentioned should be sensitive indicators of surface carboxyl and phenolic hydroxyl groups if these groups react as they do in common organic chemicals.

2. To see whether surface properties of carbon blacks can be changed by the above reactions.

3. To investigate the reactions of carbon blacks with base, both from the standpoint of reaction rate and from the standpoint of reaction equilibrium, i.e. equilibrium potentiometric titration curves.
EXPERIMENTAL PROCEDURE

Preparation of Materials

The carbon black used in this work was Black Pearl #2, an ink black furnished by Godfrey L. Cabot Inc. This carbon black was chosen because of its high surface area, 850 M²/gram, its high oxygen content, 13%, and its low ash content, 0.0%, as reported by Garten and Weiss (3). This carbon black would be expected to have a large number of surface groups, and therefore is a good carbon black to use for studying these groups. The carbon black was used as received for the base adsorption studies. It was later found that a small amount of sulfate ion could be extracted from the carbon black with water by using a Soxhlet extractor. Several of the base adsorption experiments were repeated using carbon black which had been washed for one week in a Soxhlet extractor. The results of these experiments were identical, within experimental error, with those of the experiments using unwashed carbon black.

The carbon black used for the active hydrogen determination was dried at temperatures varying from 100°C to 300°C immediately before use. It was found that a temperature of 200°C was sufficient to remove most of the adsorbed water.

The carbon black used for the decarboxylation experiments was not dried before use except when the carbon black had had
a previous treatment (i.e. lithium aluminum hydride treatment, hydrogen peroxide treatment, etc.). In these cases the carbon black was dried at 125°C in air.

The hydrogen peroxide treated carbon black was prepared by adding 100 ml. of 15% hydrogen peroxide to 5 grams of carbon black. This mixture was stirred for 4 to 5 days at room temperature. After this period, the liquid was poured off and the carbon black was dried at 125°C for at least 12 hours. This treated carbon black was stored in a tightly stoppered bottle until used.

The lithium aluminum hydride treated carbon black was prepared by adding 100 ml. of a saturated ether solution of lithium aluminum hydride, with excess solid lithium aluminum hydride added to maintain saturation, to 10 grams of carbon black and the mixture was allowed to stand for several days. After this period, water was added very slowly to the reaction mixture. Large amounts of hydrogen were always evolved when water was added indicating that there was a considerable quantity of unreacted lithium aluminum hydride in the mixture. After the excess lithium aluminum hydride was destroyed by the water, the carbon black was washed several times with a large amount of 6 N hydrochloric acid to remove the aluminum. The carbon black was then washed with distilled water until the washings showed no test for chloride ion. The carbon black was then dried at 125°C and stored in a tightly
stoppered bottle until used.

The ether used as solvent for lithium aluminum hydride in the active hydrogen determination was n-butyl ether. It was obtained from Eastman Organic Chemicals, Inc. This ether was dried with calcium chloride and distilled over sodium. The fraction used boiled at 142 ± 1°C. It was then stored over sodium wire until used. The solution was prepared by adding more than enough lithium aluminum hydride to make a saturated solution. This solution was protected from the atmosphere and pipetted from the top as used. In all experiments a 20 fold excess of lithium aluminum hydride was used.

The solutions used in the study of the base adsorption by the carbon black were 0.1 N sodium hydroxide, 0.1 M and 0.001 M potassium chloride. The sodium hydroxide was prepared carbonate free and was protected from atmospheric carbon dioxide during storage. The potassium chloride solutions were prepared by weight using reagent grade potassium chloride. Distilled water was used in the preparation of all solutions.

Apparatus

The apparatus used in the active hydrogen determinations is shown in Figure 4. Bulb 1 is a 50 ml. flask with a 24/40 standard taper. Bulb 2 is a 25 ml. flask which is attached to
the system with a 19/38 standard taper in such a way that when the bulb is rotated, 180° the solution could run down into bulb 1. The manometer was a closed end mercury filled manometer capable of measuring pressures up to 65 cm. Water soluble ether insoluble stopcock grease was used at all joints.

To measure the volume of carbon dioxide given off at high temperatures the apparatus shown in Figure 5 was used. It consisted of the following: tube furnace for heating the sample, thermocouple for measuring the temperature of the furnace, drying tube, a cold trap and a manometer. The tube furnace was capable of maintaining a temperature of over 1000°C for long periods of time. The thermocouple was calibrated from 750° to 1300°C with an optical pyrometer. The calibration curve was a straight line which went through the points 100°C (boiling point of water) and 397.5°C (melting point of potassium dichromate). The tube in which the carbon black was heated was of fused quartz with a Vycor 24/40 taper sealed on the open end. The drying tube was filled with anhydrous calcium chloride. The cold trap was cooled with liquid nitrogen. The manometer was a closed end mercury filled manometer.

The instrument used in the kinetic study of the carbon-black-base reaction was a Carlsberg pH Stat. This instrument is a direct reading pH meter which has an arrangement by
Figure 4. Apparatus used for the active hydrogen determination
Figure 5. Apparatus used for the determination of the amount of carbon dioxide released from the carbon black upon pyrolysis.
which acid or base can be added to the solution by means of a micro syringe to keep the pH constant. The pH stat was connected to a recorder which plotted the amount of base added as a function of time. A glass-calomel electrode system was used. The reaction vessel held 8 ml. of solution and was thermostated, usually at 25°C. The suspension was stirred with a small magnetic stirrer.

All pH measurements were made by means of a Beckman Model G pH meter (glass electrode, saturated calomel reference electrode) in the preparation of the equilibrium titration curves.

Procedures

In the active hydrogen determination, a known amount of carbon black was placed in bulb 1 and the lithium aluminum hydride solution was added to bulb 2. Liquid nitrogen was placed around bulb 2 to freeze the lithium aluminum hydride solution. After the solution had frozen, the system was evacuated for about an hour to remove the water vapor from the system. The system was not flamed out because of the danger of destroying some of the surface groups on the carbon black. Then the stopcock was closed and the liquid nitrogen removed. After the system had warmed up and the pressure reading was equal to the vapor pressure of the ether solution, (0.75 cm.) bulb 2 was rotated to allow the solution to run
into bulb 1 which contained the carbon black. The pressure was read at various time intervals until the rate of change of the pressure with respect to time was very small. It was observed that the pressure never reached a constant value even after 3 or 4 days. However, when a blank determination was made without the presence of carbon black, the pressure reached a constant value within one hour or less.

At the start of a pyrolysis experiment, a known amount of carbon black was in the quartz tube and all stopcocks were open. The liquid nitrogen was not around the cold trap. The system was then evacuated. The furnace was heated to 300°C and kept at this temperature for several hours, usually over night. None of the gases, if any, coming from the carbon black was condensed in the cold trap during this period. Then the liquid nitrogen was placed around the cold trap, and the temperature of the furnace was raised to 1000°C. The furnace was kept at this temperature for 3 or 4 hours after which time stopcocks S1 and S2 were closed, and the liquid nitrogen was removed from around the cold trap. The system was allowed to warm up to room temperature before the pressure reading was taken.

At the start of a kinetic run, an accurately weighed sample of carbon black was in the reaction vessel with 6 ml. of 0.1 M KCl solution, the stirrer was running and base was
in the syringe. The weight of carbon black used depended on the pH at which the run was made. At high pH a larger amount of base is adsorbed by the carbon black and hence a smaller amount of carbon black was used than at a lower pH. When the carbon black was added to the KCl solution, the pH of the solution dropped from 6.5 to 2.9 in a few minutes. After enough time was allowed for this initial pH to be attained, the pH stat was set at the proper pH and turned on. The instrument then recorded automatically base added as a function of time.

The titration curves were obtained by measuring the pH of suspensions of carbon black as function of amount of base added. In the case of the curve prepared at an ionic strength of 0.1 M, 50 ml. of 0.1 M KCl was added to several small flasks each containing an accurately weighed sample of carbon black. The sample size was usually about 0.5 grams. To these flasks were added varying amounts of sodium hydroxide. They were then stoppered and shaken occasionally over a period of one week. At the end of this time, the contents of the flasks were poured into beakers, and the pH of the supernatent liquid was measured. The same procedure was followed for the 0.001 M curves except that the total volume of the mixture was 500 ml. and the amount of the carbon black was reduced to about 0.25 grams.
EXPERIMENTAL RESULTS

Dependence of active hydrogen content of carbon black on surface treatment, as determined from the hydrogen evolved on reaction with lithium aluminum hydride, is presented in Figures 6 and 7. These show, for each treatment, the amount of hydrogen evolved per gram of carbon as a function of time.

Results of equilibrium base adsorption experiments are presented in Tables 1 and 2, and graphically in Figure 8.

Dependence of base adsorption on time and stirring rate at pH 7 is presented graphically in Figure 10.

Results of the pyrolysis experiments on the variously treated carbon blacks are presented in Table 3.
Table 1. Equilibrium base adsorption at 0.1 M ionic strength

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Table 2. Equilibrium base adsorption at 0.001 M ionic strength

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<tr>
<td>9.00</td>
<td>695</td>
</tr>
<tr>
<td>9.28</td>
<td>790</td>
</tr>
</tbody>
</table>
Table 3. Amount of carbon dioxide released by the carbon black upon pyrolysis

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Millimoles of CO₂ per gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated carbon black</td>
<td>1.30</td>
</tr>
<tr>
<td>LiAlH₄ treated carbon black¹</td>
<td>1.65</td>
</tr>
<tr>
<td>LiAlH₄ treated carbon black²</td>
<td>1.62</td>
</tr>
<tr>
<td>Water treated and dried at 125°C</td>
<td>1.52</td>
</tr>
<tr>
<td>H₂O₂ treated</td>
<td>2.70</td>
</tr>
<tr>
<td>H₂O₂ treated³</td>
<td>2.30</td>
</tr>
</tbody>
</table>

¹Dried at 125°C in air.
²Vacuum dried at room temperature.
³Another sample of H₂O₂ treated carbon black.
Figure 6. Active hydrogen content of the carbon black as function of time at different predrying temperatures
Figure 7. Amount of active hydrogen released by the carbon black upon treatment with lithium aluminum hydride as function of time and previous treatment of the carbon black.
Figure 8. Equilibrium titration curves of the carbon black at 0.1 M and 0.001 M ionic strength

Figure 9. Equilibrium titration curves after application of the correction for the potential drop across the diffuse part of the double layer due to change in ionic strength
Figure 10. Rate of base adsorption as function of time at different stirring rates
DISCUSSION

Figures 6 and 7 show the time-dependent hydrogen evolution resulting from the reaction between lithium aluminum hydride and variously treated carbon blacks. The evolution of hydrogen was very rapid during the first few minutes, but slowed down to a relatively slow rate after two or three hours. As shown by Figure 6, the evolution does not completely stop, but continues at a more or less constant rate for several days. For this reason it is not possible to obtain an exact value for the active hydrogen on the carbon black by this method.

This work is primarily concerned with the properties and reactions of the surface groups on carbon black. The lithium aluminum hydride reaction evidently reflects sensitively different surface treatments of the carbon blacks, although (because definite completion of the reaction was not indicated) the absolute change in number of groups resulting from the treatments cannot be ascertained by this method. The method as used does not distinguish between carboxyl, phenol, or alcohol groups or adsorbed water molecules.

The temperature at which the carbon black is dried and the way it is stored and handled has some effect on the amount of hydrogen released. This is illustrated by the curves for carbon blacks dried at 100°C and 300°C before
reaction with lithium aluminum hydride. This difference, about 8%, is assumed to be due to different amounts of adsorbed water. Unless special care is taken in drying, weighing and handling of the carbon black, the curves will not be exactly reproducible. The changes in the active hydrogen content of the carbon black due to the various treatments are expected to be large. For this reason the changes in the active hydrogen content due to the hydrogen peroxide treatment or the lithium aluminum hydride treatment are not believed to be significant.

Lithium aluminum hydride is a good reducing agent for organic compounds. It will reduce carboxylic acids, acid chlorides and esters of carboxylic acids to alcohol groups. It will also reduce quinones to hydroquinones and carbonyl groups to alcohols. Therefore, lithium aluminum hydride treatment of carbon black may affect the active hydrogen content of the carbon, but the direction of the total effect cannot be predicted; active hydrogens will be removed by reduction of carboxyl groups (if the alcohol groups formed are insufficiently acidic to react with lithium aluminum hydride during the allowed reaction periods) but additional active hydrogens will be generated by reduction of quinone and carbonyl groups (if the alcohol groups formed are sufficiently acidic to react). In fact, no significant change in the amount of active hydrogen (as determined by the
lithium aluminum hydride reaction) resulted from a preceding lithium aluminum hydride treatment.

The fact that neither the hydrogen peroxide treatment nor the lithium aluminum hydride treatment has an effect on the active hydrogen content of the carbon black indicates that either no change in the carbon black resulted from the above treatments or that the active hydrogen method cannot be used as a method to measure these changes. Therefore, experiments were performed in which the amount of carbon dioxide released was measured when the carbon black was heated to 1000°C in a vacuum. It was found that this quantity was very reproducible for a given sample of carbon black. Carboxyl groups on the surface of the carbon black should release carbon dioxide when heated to this temperature. It is also conceivable that other reactions or groups could affect the quantity of carbon dioxide released. Peroxide groups on the carbon would be expected to give carbon dioxide, carbonyl or hydroxyl groups close to each other on the surface could interact to release carbon dioxide. Carbon dioxide can react with the carbon black surface to give carbon monoxide and a surface oxygen complex. Many such reactions can be proposed which would affect the amount of carbon dioxide released by a carbon black on pyrolysis. Which of these reactions are the principal sources of carbon dioxide cannot be stated on the basis of these experiments alone. Therefore, it
is assumed for this work that the amount of carbon dioxide released from carbon black at high temperatures is a property of the functional groups on the carbon black surface and furthermore that changes in this quantity can be interpreted as changes in the functional groups on the carbon black surface. The experimental observations obtained will be interpreted on this basis.

When the carbon black is treated with hydrogen peroxide the amount of carbon dioxide released by the carbon black on pyrolysis is greatly increased. Hydrogen peroxide can act as an HO⁺ donor in the presence of an acid. The carbon black surface has many acidic groups which could promote this reaction. The HO⁺ ion can attack a benzene ring much like R⁺ and Br⁺. The resulting substituted ring is much more susceptible to further addition than the unsubstituted ring. When two or more hydroxyl groups are on the same ring, there is a possibility that the ring can be oxidized by hydrogen peroxide to a quinone or some other highly oxidized system. Behavior of these groups on pyrolysis cannot be predicted with certainty, but it does not seem unreasonable to expect that some of these groups would release carbon dioxide when they are heated to a high temperature. The fact that the amount of active hydrogen released by the carbon black was unchanged may well have been an accident. Some hydroxyl groups are removed by oxidation and some new hydroxyl groups are formed
by addition. It would also be possible to explain why 2.7 millimoles of carbon dioxide was released upon pyrolysis in one case and 2.3 millimoles of carbon dioxide in another by assuming that in the first case the oxidation had progressed to a greater degree.

The results of the lithium aluminum hydride treatment are not as easily explained. Neither the active hydrogen content nor the amount of carbon dioxide released at high temperatures was changed by treatment of the carbon black with lithium aluminum hydride. There are two possible ways to explain the above results, neither of which is entirely satisfactory. If there are no carboxyl groups on the surface of the carbon black, no reduction can take place and no effect due to lithium aluminum hydride treatment would be expected. This explanation is difficult to justify in the light of the evidence presented by Studebaker et al. (2). Studebaker and his associates were able to produce two types of esters on carbon black by treatment of the carbon black with diazomethane. One of these types could be hydrolyzed with dilute acid and the other could not. The ester that could be hydrolyzed with dilute acid was assumed to be due to reaction of the carboxyl groups on the carbon black surface with the diazomethane.

It is also possible that there are carboxyl groups on the surface of the carbon black but these carboxyl groups are
either not reduced by lithium aluminum hydride or once reduced are themselves very good reducing agents. In order to obtain the carbon black free from the lithium and aluminum, it is necessary to wash the carbon black with a large volume of acid to wash out the aluminum and then with a large volume of pure water to remove the acid. After the carbon black was washed, it was air dried at 125°C. Strong reducing agents if formed by the original lithium aluminum hydride treatment might well be reoxidized by this treatment. Functional groups expected from the proposed model to be formed from the reduction (alcohol, hydroquinone) would not be expected to be oxidized by air at 125°C when present in conventional organic chemicals, however.

In several of the attempts to prepare a reduced carbon black with lithium aluminum hydride, a carbon black was obtained which released more carbon dioxide than the untreated carbon black. It was also found that mere wetting of the untreated carbon black and drying it at 125°C produced a carbon black which released more carbon dioxide than the untreated carbon black. It appears that oxygen in the presence of water can oxidize some of the functional groups on the carbon black surface. This suggests a peroxide reaction mechanism. This is also in agreement with the fact that hydrogen peroxide is able to greatly increase the carbon dioxide released at high temperatures. At no time was it
possible to reduce the amount of carbon dioxide released by chemical treatment of the carbon black.

Treatment of the carbon black with diozomethane lowered the active hydrogen of the carbon black as expected; according to the model proposed, this treatment should produce esters from carboxyl groups, ethers from hydroxyl groups.

High temperature treatment of the carbon black should pyrolyze functional groups and thus reduce the number of active hydrogens; hydrogen evolution curves (Figure 6) resulting from the reaction between lithium aluminum hydride and carbon blacks outgassed at 600°C and 1000°C confirm this expectation.

Acidic (e.g. carboxyl, phenolic) groups on the surface of carbon black may be expected to donate protons to base leaving the surface negatively charged. If, as in the present study, the base is hydroxide ion, physical or chemical adsorption of base, while believed less probable than the reaction just described, could not be distinguished from it in aqueous solution. The pH at which the carbon black surface is uncharged is not known, but it is presumed to be quite low for the carbon black used in this work. At any higher pH the carbon black surface will be negatively charged, and it is believed to be negatively charged over the entire range of titration curves covered in the present work.
Since the carbon black surface is negatively charged, there will be a layer of positive charges very close to the surface. This double layer of charges is known as the electrical double layer. Since the surface is charged, and the solution is neutral, there must be a potential drop across the electrical double layer. Figure 11 is a representation of the Gouy-Stern model of the potential drop across the electrical double layer. The surface potential depends on the charge on the surface and the capacity of the double layer. In general,

\[ Q = CV \]

where

- \( C \) = the capacity of the double layer per unit area
- \( V \) = the surface potential
- \( Q \) = the charge per unit area.

In the case of carbon black,

\[ Q = \frac{Fr}{A} = \frac{F(r_o + b)}{A} \]

where

- \( F \) = the faraday constant
- \( r \) = the number of groups ionized
- \( r_o \) = the number of groups ionized before base is added
- \( b \) = the amount of base adsorbed
- \( A \) = the surface area of the carbon black.

The pH of the solution is a measure of the potential
Figure 11. Gouy-Stern model of the potential drop across the electrical double layer.
difference between the solution and the surface. The relation between pH and potential is

\[ V = 0.059(pH - pH_{zpc}) \]  

\( pH_{zpc} \) is the pH at which the surface of the carbon black is uncharged. By combining equations 1, 2 and 3, one obtains

\[ \frac{F(r_0 + b)}{A} = 0.059(pH - pH_{zpc})C \]  

A differential capacity can be calculated from the slope of the titration curve. Differentiating and rearranging equation 4 gives

\[ \frac{db}{dpH} = \frac{0.059AC}{F} = kC \]

The slope of the titration curve is \( dpH/db \). It can be seen from equation 5 that if the capacity of the double layer is constant, \( db/dpH \) must also be constant and hence the titration curve (pH plotted against base adsorbed) will be a straight line. The titration curve shown in Figure 9 is indeed straight over a wide range. The capacity calculated from this line is 29 microfarads per square cm. This compares favorably with the capacity of silver iodide and mercury surfaces in that they are of the same order of magnitude; the capacity at the mercury-0.1 N NaF solution interface varies from 29 to 15 microfarads per square cm. as reported by Grahame (9) and the capacity of the silver iodide-0.1 N NaClO₄ interface varies from 32 to 13 microfarads per square
cm. as reported by Mackor (10).

At high surface charge the titration curve indicates that the capacity of the double layer increases greatly with increase of surface charge. This can be explained qualitatively in two ways. When the surface has a high negative charge, there is a large force exerted on the positive ions in the solution. This tends to compress the double layer which would increase the capacity just as the capacity of a parallel plate condenser is increased as the plates are moved closer together.

Alternatively, the increase in capacity of the electrical double layer at high pH may reflect the nature of the groups responsible for base adsorption. The groups on carbon black surfaces most likely to react with base are carboxyl groups and phenol groups. Carboxyl groups are much more acidic than phenol groups and would be expected to react with base at a lower pH. If it is assumed that only carboxyl groups react at low pH, a linear relationship would be expected when the surface charge is plotted against the surface potential, provided that the double layer capacity remains constant. This is equivalent to plotting pH against b. At sufficiently high pH, phenolic groups would be expected to react with base, increasing the number of sites which can be charged by adsorption of base. Therefore, addition of more base would result in the ionization of more phenol
groups increasing the surface charge without increasing the pH very much.

The above assumption is supported by the fact that about 2.6 millimoles of active hydrogen were released upon treatment of the carbon black with lithium aluminum hydride and only about 1.3 millimoles of carbon dioxide were released upon pyrolysis of the carbon black. This indicates that a large part of the active hydrogen on the carbon black is due to groups other than carboxyl groups. These may well be phenolic groups.

At any given pH there will be a fixed surface potential $\mathcal{M}_0$. Refer to Figure 11. At very low ionic strength, the $\mathcal{M}_d$, potential drop across the diffuse part of the double layer, will be large. Therefore, $\mathcal{M}_c$ (the potential drop across the compact part of the double layer) will be small. At high ionic strength, $\mathcal{M}_d$ will be small and $\mathcal{M}_c$ will be large.

It is proposed that the capacity of the compact double layer is independent of the ionic strength, since it is considered to be free of ions. Therefore

(1) \[ Q = CV \]

can be replaced by

(6) \[ Q = C(\mathcal{M}_0 - \mathcal{M}_d) \]

in which $Q$ is the function of $\mathcal{M}_0 - \mathcal{M}_d$, independent of electrolyte concentration. Therefore,

(7) \[ C = \frac{Q}{\mathcal{M}_0 - \mathcal{M}_d} \]
in which \( C \) is also independent of electrolyte concentration. Therefore, if instead of plotting \( Q \) against \( V \) (which is equivalent to plotting \( b \) against \( \text{pH} \)) one plots \( Q \) against \( \bar{V}_o - \bar{V}_d \), one should obtain a curve which is independent of ionic strength. The value of \( Q \) is known except for an additive constant (\( r_0 \) in previous notation); \( r_0 \) is estimated from the \( \text{pH} \) of a carbon black slurry in absence of added base.

The quantity \( \bar{V}_d \) can be calculated from

\[
(8) \quad \sinh 19.46 \bar{V}_d = \frac{Q}{11.72/\mathcal{C}}
\]

This calculation was performed for the titration curves in which 0.1 M KCl and 0.001 M KCl solutions were used as the supporting electrolyte. Figure 8 shows the position of the titration curves before the correction was applied and Figure 9 shows the position of the curves after the correction was applied. Evidently the procedure discussed has greatly over-corrected for the ionic strength effect, although the correction has been in the right direction. The overcorrection may result from an overestimation of \( r_0 \) and hence of \( Q \); available data do not permit an objective estimation of \( r_0 \) other than that used.

The above electrical double layer approach used in the interpretation of the base adsorption data is interesting because the calculated double layer capacity is in the same
range as the capacity of the other well-studied systems. Another interesting method of interpreting the data is very similar to the approach Tanford (11) used to explain his titration curves for proteins.

Proteins are very large complex molecules which have a number of free carboxyl, phenol, and amine groups which can react with acid or base. Tanford postulated that each type of group, for example carboxyl, has a certain pK value which is independent of the number of such groups on the molecule or the charge on the molecule. This pK value Tanford called pK$_{int}$ (intrinsic pK). The fact that the group seems to have a wide range of pK values can be explained by electrical effects determined by the charge on the molecule. This is equivalent to saying the two carboxyl groups on oxalic acid have the same pK$_{int}$, but that it is much more difficult to remove a proton from a negatively charged molecule than from one which is uncharged.

The free energy for the process of removing a proton from the surface then becomes

$\Delta F = \Delta F^0 + kZ$

where

$\Delta F^0$ = the free energy in the absence of a surface charge

$k$ = a constant

$Z$ = the charge on the surface.

By using the standard substitutions, the following equation
can be obtained.

\[(10) \quad \text{pH} - \log \frac{r}{n - r} = pK_{\text{int}} - kZ\]

where

- \(r\) = the number of groups ionized per gram
- \(n\) = the total number of groups per gram
- \(Z\) = the charge on the surface per gram
- \(pK_{\text{int}}\) = the intrinsic pK of the group

In the case of carbon black, a slight modification of equation 1 is in order. Tanford (11) knew the charge on the protein molecule from other measurements. The charge on the carbon black is not known but is assumed to be, for the sake of these calculations, \((r_o + b)\), where \(r_o\) is the number of groups ionized before any base is added and \(b\) is the moles of base adsorbed per gram of carbon black. Equation 10 then becomes

\[(11) \quad \text{pH} - \log \frac{r_o + b}{n - r_o - b} = pK_{\text{int}} - k(r_o + b)\]

The value of \(n\) is not known but as a first approximation it will be assumed equal to the amount of carbon dioxide evolved by the carbon black upon pyrolysis. Using these assumptions about \(n\) and \(Z\), \(\text{pH} - \log \frac{(r_o + b)/(n - r_o - b)}\) was plotted against \((r_o + b)\) (see Figure 12). A straight line was obtained which had a slope of \(k(4.85 \times 10^{-3})\) and an intercept of \(pK_{\text{int}}(4.50)\). Little can be said about the significance of the value of the slope of this line. However, the value of
Figure 12. Tanford's treatment of protein titration curves applied to the equilibrium titration curve of carbon black
4.50 for the pK_{int} is not far from the pK of acetic acid (4.75) and that of benzoic acid (4.57). The pK_{int} value obtained therefore is consistent with the model placing carboxyl groups on the carbon black surface.

From the titration curve in Figure 8, it can be seen that at surface charges above 900 micromoles per gram the titration curve departs from a straight line. The plot of pH - \log[(r_0 + b)/(n - r_0 - b)] against (r_0 + b) covers the range of (r_0 + b) from 0 to 1050. This is essentially the linear portion of the titration curve. It can be seen from equation 2 when (r_0 + b) becomes very close to the value of n, the log term becomes very large, which means that the pH must rise sharply with increasing surface charge if equation 2 is going to produce a straight line. When (r_0 + b) becomes greater than n, (r_0 + b)/(n - r_0 - b) becomes negative and the log term no longer has any physical meaning.

To remove the above difficulty, it was assumed that base-adsorbing groups other than carboxyl (e.g. phenol) were also present. Other evidence (i.e. active hydrogen, pyrolysis) also indicates the presence of such groups. The charge Z then becomes (r'_0 + r_0'' + b) and equation 11 becomes

\begin{equation}
\text{pH} = \log \frac{r_i}{n_i - r_i} = pK_i + kZ \quad (i = 1, 2)
\end{equation}

\begin{equation}
r_i = \frac{n_i K_i 10^{pH-k(Z)}}{1 + K_i 10^{pH-k(Z)}}
\end{equation}
(14) \[ r_1 + r_2 = (r'_o + r''_o + b) \]

\[ = \sum \frac{n_1 K_1 10^{PH-k}(r'_o + r''_o + b)}{1 + K_1 10^{PH-k}(r'_o + r''_o + b)} \]

By introducing equation 14 into equation 12 and assuming \( r''_o = 0 \), the following equation is obtained

(15) \[ pH = \log \left( \frac{r_o + b}{n_1} \right) \left( 1 + K_1 10^{PH-k'}(r_o + b) \right) \]

\[ = pK_1 + k(r_o + b) \]

\[ - \log \left\{ 1 + \frac{n_2 K_2 (1 + K_1 10^{PH-k}(r_o + b))}{n_1 K_2 (1 + K_2 10^{PH-k}(r_o + b))} \right\} \]

(16) \[ \frac{1 + K_1 10^{PH-k}(r_o + b)}{n_1} = \frac{1}{n - r_o - b} \]

For all values of \((r_o + b)\) above 1000, the term \(10^{PH-k}(r_o + b)\) was small in comparison to unity. Therefore equation 15 reduces to equation 11 except that the term \( \frac{1 + K_1 10^{PH-k}(r_o + b)}{n_1} \) never becomes negative and so the logarithm of a negative number is not encountered. However, equation 15 does not fit the data any better than equation 11, and like equation 11, predicts a more rapid increase in pH with addition of base than is observed.
A simple experiment was conducted to show qualitatively that the rate of base adsorption was strongly dependent on stirring rate. In this experiment, base was added automatically to keep the pH constant, and a magnetic stirrer adjusted manually to achieve stirring rates characterized qualitatively as "slow" (slowest possible operation of stirrer), "intermediate" (this would correspond to a normal use of the magnetic stirrer) and "fast" (fastest possible operation of the magnetic stirrer). Operation of the stirrer at "fast" rate was erratic, and the stirrer tended to cease operation. In the course of an experiment the carbon black becomes depelletized, and thereafter it is not possible to observe the stirring visually. On this account, stirring effectiveness beyond 10 minutes is uncertain in the case of the "fast" stirring rate.

Results are presented graphically in Figure 10. Curves 1 and 2 were obtained at "intermediate", curve 3 at "fast" and curve 4 at "slow" stirring rates. Evidently the rate of base adsorption depends strongly on stirring rate. This indicates that diffusion plays an important part in limiting the adsorption rate.

This conclusion is also suggested by the finding of Weller and Young (12) that the rate of base adsorption by carbon black depended strongly on particle size.
LITERATURE CITED


10. Mackor, E. L. The properties of the electrical double layer III the capacity of the double layer on Hg and on AgI. Rec. Trav. Chim. 70:763-783. 1951.
