

6. *Studies in Chemisorption on Charcoal. Part II. Experiments on the Formation of the Acid Constituent of Charcoal.*

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In Part I (J., 1933, 842), the formation of small quantities of an organic acid, probably oxalic acid, in ash-free charcoal was reported; and it was shown that the acid was formed only if the charcoal had been exposed to oxygen. The following experiments were carried out with a view to discover the conditions of the formation and to investigate the complex on the surface of the charcoal which gave rise to it.

There is some evidence that charcoal retains a small amount of water vapour irreversibly adsorbed. This residual moisture must be firmly held at centres of high adsorption potentials similar to those at which oxygen might be assumed to be chemically attached to the carbon. Its removal might be assumed to exert some influence on the binding of the oxygen, or at least on the quantity of oxide formed, as determined by estimation of the oxalic acid produced from it.

An investigation of the effect of drying on the adsorption of oxygen in charcoal was carried out by C. J. Baker (J., 1887, 51, 249), a repetition and extension of whose work constitutes the latter part of the present paper.

EXPERIMENTAL.

The amounts of oxalic acid in the various extracts were determined directly by titration in acid solution with *N*/100-potassium permanganate, prepared immediately before use by dilution of a stock *N*/10-solution and standardised against sodium oxalate. The burette used was N.P.L. tested and measured accurately to 0.01 c.c.

In conjunction with every series of titrations of dilute oxalic acid solutions from the charcoal, a blank titration was carried out with the same volume of water and the same acidity as in the actual analysis; the volume of permanganate required in the blank titrations was an appreciable fraction of that used in the determination of the small amount of oxalic acid, *e.g.*, for extract, 0.89 c.c.; for blank, 0.13 c.c. The results were all corrected for the blank and calculated to exactly *N*/100-potassium permanganate, so that 1 c.c. \equiv 0.63 mg. $C_2H_2O_4 \cdot 2H_2O$.

(1) *Passage of oxygen through suspensions of charcoal in water.* A sample of 3 g. of the pure charcoal, evacuated at red heat and weighed in nitrogen, was put into each of six boiling tubes containing 25 c.c. of water. The tubes were connected in series by means of glass tubing and a slow current of oxygen was passed through them. The state of division of the charcoal was sufficiently fine and the stream of oxygen sufficiently rapid to keep the charcoal in violent agitation and to ensure that its whole surface came into contact with the gas. The end tube was detached after oxygen had been passing for 1 minute, the second after 5 minutes, the third after 30 minutes, and so on. The temperature throughout this and the following experiments was 16–18°. The contents of each tube were rapidly filtered as soon as it was detached, and the filtrate titrated immediately. The following results were obtained :

Time of passage of O_2 , mins.	1	5	30	60	180	720
<i>N</i> /100- $KMnO_4$ required, c.c.	0.69	0.62	0.71	0.73	0.69	0.71

(2) *Effect of bubbling air.* Similar experiments were carried out with air instead of oxygen. The average titration value was 0.72 c.c. and was again independent of the time of passage.

(3) *Effect of the use of different quantities of charcoal.* Samples of charcoal varying from 0.1 to 4 g. were weighed into tubes, 40 c.c. of water added in each case, and the tubes mechanically shaken for 3 hours. The amount of oxalic acid in each solution was then determined, as follows :

Wt. of charcoal, g.	0.121	0.571	1.232	1.787	2.362	3.514	3.997
<i>N</i> /100- $KMnO_4$ required, c.c.	0.03	0.15	0.33	0.48	0.62	0.93	1.07

(4) *Treatment of charcoal with aqueous alcohol.* Further 3-g. samples of charcoal were shaken in tubes with 20 c.c. of alcohol-water mixtures varying in concentration from 0 to 100% alcohol. After being shaken for 3 hours, the contents of each tube were filtered and titrated, a further 10 c.c. of water having been added to each filtrate. The following results were obtained :

Concn. of soln. : alcohol, %	0	25	50	75	90	95	100
<i>N</i> /100- $KMnO_4$ required, c.c.	0.83	0.79	0.89	0.78	0.81	0.79	0.00

(5) *Treatment of moist charcoal with oxygen under pressure.* Weighed samples of moist charcoal were placed in a steel cylinder with a needle valve. Oxygen was produced in the closed cylinder under a calculated pressure by means of the action of water on sodium peroxide, the cylinder being warmed. After some time, the pressure of oxygen in the cylinder was released and the charcoal washed out and well shaken with water. After filtration, the extract was titrated for oxalic acid. Although pressures of oxygen up to 20 atm. were used, the quantity of oxalic acid was in each case the same as that formed at atmospheric pressure.

(6) *Regeneration of oxalic acid in samples of charcoal.* To each of two 3-g. samples of charcoal, 20 c.c. of water were added, and the containing tubes well shaken for 3 hours, the filtrate from each sample being then titrated: 0.79 and 0.81 c.c. of *N*/100-permanganate were required. The first sample of charcoal was immediately reshaken in air without drying and after the addition of a further 20 c.c. of water; the filtrate after this treatment required only 0.42 c.c. of permanganate. The second sample of the charcoal was dried by heating in air at 120° for an hour and was then re-treated in the same way as before. The titration was in this case 0.84 c.c., approximately the same as the original value.

(7) *Use of activated charcoal.* 3-G. samples of birchwood charcoal, which had been activated for different times at a high temperature and then reheated in air for some time to dull redness, were treated with water and shaken in air in exactly the same way as above. The titration values were somewhat different from that obtained from the same weight of purified sugar charcoal but were of the same order, the average volume of *N*/100-permanganate being 1.02 c.c. The values varied irregularly amongst themselves and were not dependent on the time of activation.

(8) *Effect of organic solvents on the charcoal.* Samples of 2–3 g. of charcoal were superficially dried by heating in a current of air for a few hours at 100°, shaken in stoppered bottles with dried solvents for 3 hours, and then filtered. The following solvents were used: ethyl alcohol, ether, benzene, acetic acid, chloroform, carbon disulphide, methyl alcohol, acetone, and xylene. The filtrates were then evaporated to dryness, but in no case was there any residue whatsoever. (Oxalic acid is fairly soluble in alcohol and sparingly soluble in some of the other solvents used.) Similar extractions with charcoal that had been left in the air for a few hours but had not received any preliminary drying also gave negative results.

(9) *Experiments with dried charcoal.* In his experiments on the effect of drying on the adsorption of oxygen on charcoal, C. J. Baker attempted to get rid of the last traces of moisture by heating the charcoal at 150° for a week. Another sample was further dried by heating at 35–40° for 2 months, and then gave results slightly different from those of his main experiments. In view of this, and of the general difficulty of drying porous substances, more thorough drying than the above seemed advisable.

The apparatus in which the drying was carried out was constructed entirely of Pyrex glass which had been especially chosen as being free from capillaries and was thoroughly baked out before use. The charcoal, which had been given a preliminary drying, was placed in bulbs with entrance and exit tubes arranged so that the gas used to dry the charcoal should pass through it and not over it. The charcoal was first evacuated at a dull red heat. Nitrogen which had been freed from oxygen and dried by bubbling through sulphuric acid and then passed through several yards of phosphoric oxide drying tubes was allowed to enter the apparatus gradually, and a slow stream passed for 6 weeks, during which the charcoal tubes were evacuated and heated to redness twice daily. The charcoal was now thoroughly evacuated once again at a red heat, and oxygen which had been thoroughly dried with phosphoric oxide allowed to pass through it slowly for 3 days. Three of the four bulbs of charcoal that had been dried were now sealed off, and the fourth, which was connected to an apparatus for the collection and analysis of gases, was evacuated and its temperature gradually raised. At 100° there was no trace of any gas evolved, and none was noticed until the temperature had reached about 350°, whereupon small traces of carbon monoxide began to come off. At about 470° a rush of gas began, and on further rise of temperature smaller amounts of gas were slowly evolved. There was no indication whatsoever either of any lower oxide of carbon or of free oxygen. The gas obtained was almost pure carbon monoxide, there being only traces of the dioxide.

Another of the bulbs of dried charcoal which had been sealed off was now opened by breaking a side tube, and water, from which all the air had been boiled out, was allowed to enter. The charcoal was well shaken and filtered out of contact with the air. The filtrate was evaporated to 20 c.c., acidified, and titrated with *N*/100-permanganate. The amount required was 0.07 c.c. (from 4 g. of charcoal), a quantity smaller even than that obtained on extraction of a charcoal from which the oxygen had been out-gassed and replaced by nitrogen, and therefore negligible.

Another bulb of dried charcoal was broken, and dilute sulphuric acid sucked in. The filtrate from this was tested with a few drops of starch-iodide solution, which gave no coloration, even on standing.

DISCUSSION.

The experimental results show that the formation of oxalic acid in the pores of charcoal is remarkably unaffected by variations in the conditions. The amount of acid formed was directly proportional to the weight of charcoal used in the extraction with a constant volume of water, thus affording additional evidence that the acid is formed in the pores of the charcoal rather than by the direct action of water and oxygen on the solid carbon.

Increase in pressure of oxygen had no effect on the amount of acid formed on a given area of charcoal surface and decrease in the partial pressure of oxygen by the use of air (and in later experiments by the use of still more dilute oxygen-nitrogen mixtures) had no measurable effect. The material giving rise to the oxalic acid must therefore be formed almost instantaneously by a preferential adsorption on or combination with the more active portions of the charcoal surface.

The effect of water concentration is equally slight, concentrations of water as low as 5% being capable of producing the same amount of oxalic acid as conductivity water. Absolute alcohol, on the other hand, does not extract the acid from the charcoal, although oxalic acid is readily soluble in it. A small minimum amount of water is therefore apparently necessary to react with the surface complex to produce acid, or if carboxyl groups are already present, to wash them off as oxalic acid.

In the experiment on the regeneration of acid from samples of charcoal from which it had already been extracted, it was found that the original amount was obtained only if the charcoal had been dried between the extractions; the smallness of the quantity formed otherwise was probably due to the fact that the smaller capillaries were full of water which did not allow the access of a fresh supply of oxygen.

The samples of charcoal used adsorbed approximately ten times their own volume of oxygen. Calculation shows that only about 0.5% of this oxygen is used in the formation of the acid, and if it be assumed that the oxygen forms a unimolecular layer on the surface of the charcoal, only a small fraction of this surface will be available for the formation of the acid. It is noteworthy that Rideal and Wright (J., 1925, **127**, 1347) found that only about 0.38% of a charcoal surface was available for autoxidation, this being of the same order as that which produces the oxalic acid.

If these parts of the surface, active for the formation of the acid, were distributed irregularly over the charcoal, it would be expected that activated charcoal whose surface was much greater than that of the sugar charcoal used, should produce a much larger amount of acid. Experiments show, however, that the amounts of acid formed in activated and in unactivated charcoal are of the same order, the ratio of the quantity of oxygen used in the formation of the acid to that normally adsorbed being, if anything, less in the activated samples. It is logical to assume, therefore, that the acid is formed at pits and peaks in the charcoal surface, and that activation, which is accompanied by an extension of the surface generally, does not mean an increase in these regions of greater activity.

Neither by extraction of charcoal with a series of solvents nor by distillation of the dried substance was it possible to obtain even a trace of any lower oxide of carbon; so unless the surface oxide decomposes very easily, it is improbable that it exists as a definite compound except in contact with the body of the charcoal. This is to be expected from the general (Langmuir) theories of adsorption.

The oxygen on the surface of the dried charcoal is bound more firmly than that on the normal material, from which some at least can be recovered as oxides of carbon at as low a temperature as 100°. The lowest temperature at which it is given off in any quantity from the dry material is 470°, the slight difference in temperature between this and Baker's result being probably due to a slightly higher degree of dryness in the present case. This was also indicated by the fact that in the present investigation only traces of carbon dioxide were present in the issuing gases; from Baker's most thoroughly dried sample of

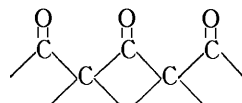
charcoal (2 months) 1.08% was present, and from his other samples (1 week) 11.28—27.7% of carbon dioxide.

These two facts—the higher temperature of gas evolution and the predominance of carbon monoxide—indicate some fundamental difference in the way in which oxygen is held on dry and on ordinary charcoal. This is further emphasised by the facts that no oxalic acid was formed on the interaction of the “dry” surface oxide with water, and no hydrogen peroxide on extraction with dilute acids.

The essential complexity of the chemical nature of the ordinary, undried charcoal surface is evident from the first series of experimental results reported above. We have to distinguish at least two types of surface: first, the main surface whose oxygen complex goes off as carbon dioxide on heating, and secondly, a small, specially active surface on which a complex is formed which gives rise to oxalic acid. The experimental evidence shows that both types of combination are changed by the removal of water from the charcoal.

The lack of acid formation suggests that the complex formed at the most active parts of the charcoal surface is entirely different from that on the undried charcoal, and the fact that no hydrogen peroxide can be obtained suggests the absence of the true peroxide structure, and hence the two formulæ $-C-O-O-$ and $\begin{array}{c} O-O \\ | \quad | \\ C \quad C \end{array}$ previously put forward for the

chemisorption of oxygen on undried charcoal are invalid. It seems possible therefore that the oxygen is attached to the carbon in the dried charcoal by a double bond over the surface generally, as in the annexed formula, which is that originally suggested by Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1154) to explain the effect of oxygen as a catalyst poison in the carbon dioxide-carbon reaction. It is also one of the formulæ suggested by Garner and McKie (J., 1927, 2455) from thermochemical data.



Such a formula would represent all the reactions of the present surface compound; it would desorb as carbon monoxide and not as the dioxide; it would neither give rise to oxalic acid with water nor form hydrogen peroxide with dilute acids. The formula suggested for this surface oxide is also that proposed by Shilov (*Z. physikal. Chem.*, 1930, **148**, 233) for his basic oxide B, which he believed to be present on normal active charcoal. There is no reason for supposing it to be absent from the undried charcoal, which must, however, also contain oxygen linked in one of the other ways indicated, which can give rise to the peroxide.

For the formation of the compound suggested above, a complete dissociation of the oxygen molecule will have to take place, and only the most active spots of the charcoal will be expected to be able to cause this. In the normal, undried charcoal it is possible that these active centres are occupied by a small proportion of water vapour held irreversibly. The normal energy of dissociation of $H_2O \rightarrow H + OH$ is 111 kg.-cals., corresponding to 162 kg.-cals. for the dissociation of the oxygen molecule into atoms; so the irreversibly retained water in ordinary moist charcoal may be bound to the carbon at high adsorption potential as H and OH. In this undried charcoal, too, at least some of the oxygen is adsorbed in the molecular state to form the complex which gives rise to the peroxide. Such oxygen would be sufficiently active to oxidise C-H or C-OH groups to the carboxyl group, and oxalic acid would be a normal product of the reaction. The proximity of active oxygen of the C-O-O- type might be expected to produce carboxyl groups directly on the surface of the charcoal, but it was not possible to detect any oxalic acid on extraction of the charcoal with alcohol. With an excess of water, however, the carboxyl groups are washed off the surface as oxalic acid, or, if the carboxyl groups are not already formed, the active group is brought into intimate contact with the adsorbed hydrogen and hydroxyl groups, and oxidation thus effected.

In the dry charcoal, on the other hand, there is no adsorbed moisture, the active centres of the carbon being occupied by doubly bound oxygen atoms. The function of the drying in inhibiting the formation of the more loosely bound oxygen complex having the peroxide structure and producing carbon dioxide on degassing is not at all clear and no explanation can be suggested at present.

The mechanism suggested above for the formation of oxalic acid by the oxidation of chemically adsorbed water seems more reasonable than the original and more obvious hypothesis that it is produced by the action of water on a carbon-oxygen complex, and is more in line with the experimental evidence.

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