# 208. Studies in Chemisorption on Charcoal. Part I. The Acid Constituent of Charcoal.

By Alexander King.

Chemisorption, the term generally applied to irreversible adsorption, was first noticed in the carbon–oxygen system. As early as 1863, Smith (*Proc. Roy. Soc.*, **12**, 424) reported that oxygen adsorbed on charcoal at room temperature underwent a chemical change and could be recovered only at higher temperatures as carbon dioxide. This was verified by other investigators (notably Baker, J., 1887, **51**, 249), some of whom also found traces of carbon monoxide in the recovered gases. Calvert (J., 1867, **20**, 293), using comparatively pure charcoal, discovered the extraordinary activity of the adsorbed oxygen, which took part with ease in many reactions which the free gas could not effect, *e.g.*, the oxidation of ethyl alcohol to acetic acid. These facts are difficult to explain on the basis of a purely physical adsorption, and hence the concept of chemisorption has arisen.

At low temperatures, oxygen is physically adsorbed on charcoal (Dewar, *Proc. Roy. Soc.*, 1904, **74**, 127) and can be recovered as such on exhaustion of the charcoal; but at higher temperatures the adsorption is irreversible and only oxides of carbon can be obtained. This difference in the types of adsorption at different temperatures is also clearly shown by the variation of the heats of adsorption with temperature (Garner and McKie, J., 1927, 2451). Similar behaviour is exhibited by other systems; *e.g.*, adsorption of hydrogen or carbon monoxide on copper or zinc oxides is reversible at ordinary but irreversible at higher temperatures.

A study of the carbon–oxygen reaction at higher temperatures leads to similar conclusions. Rhead and Wheeler (J., 1910, **97**, 2178) found that " in no case where the rate of reaction could be measured was there a primary formation of carbon monoxide." They therefore suggested that the oxygen was first held to the carbon as a " loosely fixed physico-chemical complex to be regarded as $C_xO_y$." More recently, Lowry and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1408) have found evidence for a slow reaction between carbon and oxygen at the ordinary temperature, resulting in the formation of a stable non-volatile oxide, which splits up on heating into carbon monoxide and dioxide.

Rideal and Wright (J., 1925, **127**, 1347) assume, from the different behaviour of oxygen adsorbed in charcoal at different temperatures, that there are at least three surface oxides: one removable at high temperatures as oxides of carbon, a second removable on evacuation as carbon dioxide or on fusion with alkali as carbonate, and a third removable at low temperatures as oxygen.

There is little direct evidence for the existence of surface oxides, except that of Shilov and his co-workers (*Z. physikal. Chem.*, 1930, **148**, 233), who have investigated the properties of thoroughly out-gassed charcoal, and especially its power of adsorbing electrolytes (in particular, acids) from solution, in relation to the pressure of oxygen. From the form and position of the isotherm representing the adsorption of hydrogen chloride, they deduce the existence of two basic oxides on the surface of the charcoal. They find, further, that when the charcoal is heated to 400—700°, a third, acidic oxide is formed (*Z. physikal. Chem.*, 1930, **149**, 211). After the present work was started, Kolthoff (*J. Amer. Chem. Soc.*, 1932, **54**, 4473) found evidence for acidic properties in charcoal.

Now, according to the conditions of formation, it ought to be possible to obtain more direct evidence for the existence of these oxides. In 1930, Professor H. B. Baker treated a sample of sugar charcoal with solid carbon dioxide under pressure and noticed that the aqueous extract deposited a small crystalline residue on evaporation to dryness. The investigation of this deposit formed the starting point of the present work, and it was found that the deposit was oxalic acid and was due, not to the action of the carbon dioxide on the charcoal, but to previous exposure of the charcoal to the air.

## EXPERIMENTAL.

*Purification of Materials.*—The bulk of the data for the adsorption of gases and dissolved substances on charcoal is irreproducible owing to the difficulty of preparing sufficiently standardised charcoals. Those of animal or vegetable origin vary from one batch to another, and the methods of activation used by different experimenters produce surfaces of widely different character. The effects of combined hydrogen in charcoal have been widely recognised, and Miller (*J. Amer. Chem. Soc.*, 1922, **44**, 1866) has stressed the importance of rendering the charcoal ash-free. In the present work, since the presence of even the smallest amounts of impurities in the charcoal might have led to extremely misleading results, special attention was paid to the foregoing factors in the purification of the material, the method used being a variation of Miller's process for the production of ash-free charcoal (*J. Physical Chem.*, 1926, **30**, 1031).

Centrifuged coffee-sugar was slowly charred in a basin until all the volatile matter had been driven off. The mass was then ground and heated in a silica tube with a limited supply of air to 800° for 12 hours. The temperature was now decreased to a dull redness, and a stream of chlorine passed over the charcoal for a further 8 hours; the tube was then evacuated, hydrogen passed through it for an hour, and the tube again evacuated. The charcoal was now washed with distilled water, dried, reground, mixed to a paste with concentrated hydrofluoric acid in a platinum dish, and heated over a small flame until most of the acid had evaporated, the last traces of acid being then removed by stronger heating. The charcoal was next boiled with pure concentrated hydrochloric acid and filtered after dilution of the acid, this treatment being repeated, and the charcoal washed with conductivity water until free from chloride. 5 C.c. of $N/100$-potassium hydroxide, diluted with much water, were now added, the charcoal boiled, and once more washed free from soluble impurities, the washing being continued for some 24 hours after any chloride could be detected in the washings. The charcoal was finally heated in a silica tube under vacuum for two hours to 1000°, stored in stoppered bottles, and heated to dull redness in air immediately before use. Its ash content at various stages of the treatment was as follows: Before chlorine treatment, 0·13; before treatment with hydrofluoric acid, 0·17; final product, 0·00%.

In the preliminary, critical experiments, pure conductivity water was used, but as this was later found to be unnecessary, a high-grade distilled water that left no residue on evaporation was employed.

*Extraction and Examination of the Acid Material.*—(1) About 3 g. of charcoal were exposed to the air for a day, then boiled with conductivity water, filtered off, and the filtrate evaporated to dryness in a vacuum desiccator. A small deposit remained, which was seen under the microscope to consist of clusters of needle-shaped crystals.

(2) Exposure to pure oxygen instead of air yielded a deposit after similar treatment.

(3) In order to ensure that the crystalline material was not an impurity washed out of the charcoal, 3 g. of charcoal were exposed to the air and the material dissolved out and recovered by evaporation. After being dried in air and again extracted with water after a few hours, the charcoal yielded a further crystalline product. This process was repeated ten times and in each case the crystalline deposit was produced in apparently undiminished quantity, thus indicating that it was not an impurity but a substance repeatedly regenerated in the pores of the charcoal.

(4) *Analysis of the deposit.* Sufficient material was ultimately accumulated to enable the following tests to be carried out. (*a*) The crystals gave off water when gently heated, and left a white deposit which decomposed and disappeared on stronger heating. (*b*) They dissolved readily in a few drops of water and the solution had an acid reaction to phenolphthalein. (*c*) They effervesced with concentrated sulphuric acid, evolving carbon dioxide. (*d*) The solution of the crystals readily decolorised a few drops of dilute, acidified permanganate solution on warming, and also (*e*) afforded a cloudy, white precipitate with calcium chloride solution. (*f*) These qualitative tests for oxalic acid were confirmed by microanalysis (Found: C, 18·8; H, 5·0. Calc. for $C_2H_2O_4,2H_2O$: C, 19·0; H, 4·8%).

(5) Titration with *N*/100-permanganate enabled a rough quantitative estimation to be made of the amounts of oxalic acid in the various deposits (1 c.c. = 0·63 mg. of $C_2H_2O_4,2H_2O$). Expts. (1), (2), and (3) were repeated, the solutions being evaporated to about 20 c.c., acidified, and titrated, a microburette being used. In each case 3 g. of charcoal were used and in Expt. 3 the times of successive exposures to the air were varied:

| Expt. No. | Length of exposure, hrs. | *N*/100-$KMnO_4$ reqd., c.c. |
|---|---|---|
| (1) (air) | 24 | 0·60 |
| (2) (oxygen) | 24 | 0·62 |
| (3) (1st exposure) | 24 | 0·58 |
| (2nd ,, ) | 12 | 0·60 |
| (3rd ,, ) | 1 | 0·57 |
| (4th ,, ) | 1 | 0·59 |
| (3) (5th exposure) | 12 | 0·58 |
| (6th ,, ) | 1 | 0·62 |
| (7th ,, ) | 24 | 0·59 |
| (8th ,, ) | 1 | 0·60 |
| (9th ,, ) | 0·16 | 0·58 |
| (10th ,, ) | 1 | 0·57 |

It is seen that the quantity of oxalic acid is the same no matter whether the charcoal has been exposed to air or to oxygen, or whether it has undergone several successive treatments with air and water.

(6) *Use of other charcoals.* In order to see if the production of oxalic acid was limited to sugar charcoal, similar extractions were carried out with a commercial activated wood charcoal, animal charcoal, and also the very pure charcoal (Chufarov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 883) prepared by decomposing piperonal in an autoclave at 200° under a pressure of 18—20 atm., followed by heating in air to 500°. Each of these charcoals readily yielded a deposit of oxalic acid when treated with water, the quantities being approximately the same as with purified wood charcoal.

(7) *Evacuation experiments.* A further sample of 3 g. of the purified charcoal was heated in a silica tube to 850° under a high vacuum for six hours after which the tube was cooled to 100°, and nitrogen, which had been freed from oxygen by passage over heated copper turnings, allowed to enter. After standing for a few hours, the tube was evacuated at normal temperature, and boiled out conductivity water sucked in. The charcoal was well shaken with the water, and filtered off out of contact with the air. The filtrate was evaporated to dryness, and the very small deposit dissolved in a little water and titrated with *N*/100-permanganate solution. This procedure was repeated with further 3-g. samples of the charcoal, pure oxygen, carbon dioxide, nitric oxide, and nitrous oxide being adsorbed. The titration results are tabulated below.

| Gas adsorbed. | *N*/100-$KMnO_4$ reqd., c.c. |
|---|---|
| $N_2$ | 0·07 |
| $CO_2$ | 0·05 |
| $O_2$ | 0·63 |
| NO | 0·27 |
| $N_2O$ | 0·08 |

(8) "*Peroxide*" *in the charcoal.* Samples of the charcoal were shaken with dilute sulphuric acid, and the filtrate added to starch–iodide solution. After about 1 sec., the permanent dark blue colour was developed. The charcoal which had been dried in air was once more shaken

with the dilute acid, a coloration with starch–iodide being again obtained. This was repeated several times as in (3), above, and each time iodine was produced, showing the presence of a peroxide-like substance which was repeatedly regenerated on exposure of the charcoal to the air.

If the acidification was carried out in an atmosphere of nitrogen, the iodine coloration was developed as before, but if the charcoal was first thoroughly evacuated and then saturated with nitrogen, no trace of " peroxide " was to be found in the extract.

No coloration was developed in an extract with conductivity water, on subsequent treatment with sulphuric acid and starch–iodide.

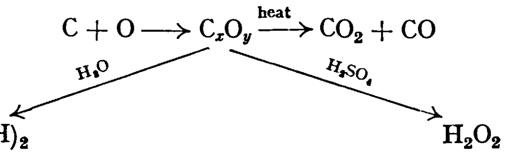
Samples of activated wood charcoal and of the pure piperonal charcoal also gave positive tests with the iodide after exposure to air and extraction as before.

## DISCUSSION.

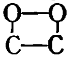
The experimental data show that, in the presence of air and water, pure charcoal is oxidised to a small extent to oxalic acid at ordinary temperatures. The fact that the quantity produced is so small indicates that the oxygen effecting the reaction is the adsorbed film on the surface of the charcoal. When the oxygen is removed by heating in a vacuum to 850° and is replaced by nitrogen or carbon dioxide, there is no oxalic acid formation, the small quantities found being probably due to a small residual quantity of adsorbed oxygen which, as is well known (see, *e.g.*, Burrage, *Trans. Faraday Soc.*, 1932, **28**, 192, etc.), is extremely difficult to remove. It is not easy to conceive of a direct action between oxygen, water, and carbon at ordinary temperatures, but, as it is known that some at least of the oxygen adsorbed by the carbon is held chemically, it seems probable that the acid is formed by the action of water on a surface oxide of carbon similar to that suggested by Rhead and Wheeler or Lowry and Hulett. Indeed, it may be identical with Shilov's acidic oxide C (*Z. physikal. Chem.*, 1930, **149**, 211). On removal of the oxide film, either by dissolution as oxalic acid or evaporation as carbon dioxide, the charcoal surface is cleaned, but on exposure to air or to oxygen the surface film of oxide is at once regenerated and can be detected in solution as oxalic acid.

It is known (Shah, J., 1929, 2660) that on exposure of charcoal to nitric oxide, chemisorption takes place, and that heating and evacuation then afford nitrogen and carbon dioxide as the main products. From Expt. 7, it seems probable that nitric oxide forms a similar surface oxide by interaction with the charcoal. Nitrous oxide, on the other hand, gave little or no indication of surface oxide formation, in agreement with Shah's finding that the adsorption of this gas was not irreversible below about 750°.

The presence of a " peroxide " on the surface of the charcoal, a phenomenon first noticed by Lamb and Elder (*J. Amer. Chem. Soc.*, 1931, **53**, 157), is in line with the other evidence and affords a third direct indication of the presence of an oxide on the surface of the charcoal. There is no reason for assuming that the " peroxide " is the same compound or complex from which the oxalic acid is derived. If it were the same substance its properties could be illustrated thus :—



The reaction with nitric oxide would be $C + NO \longrightarrow C_xO_y + N_2$ (adsorbed) $\xrightarrow{\text{heat}}$ $CO_2 + N_2$. It is not yet possible to say whether the oxide is a definite compound or is merely due to the saturation of free valencies at the active points of the carbon surface.

In all probability the mechanism of activation of carbon involves the scission of rings and chains and the exposure of free unsaturated valencies (cf. Bangham and Stafford, J., 1925, **127**, 1085). This may be done partly by oxidation, and by removal of combined hydrogen. Active patches will be produced at " peaks " in the pitted surface of the charcoal where more than one valency bond is exposed. At such a surface, oxygen might be attached, either (*a*) according to the Heitler–London mechanism, $C + O_2 \longrightarrow C{-}O{-}O{-}$, with the formation of a complex with a free valency (a surface radical); or (*b*), if the carbon valencies are symmetrically coupled, so as to form a loose valency bridge: $C{=}C + O{=}O \longrightarrow$  (Polanyi, *Z. Elektrochem.*, 1929, **35**, 561; Eckstein and Polanyi, *Z. physikal. Chem.*, *B.*, 1932, **15**, 334). It is possible that both these mechanisms come into play in at least the initial stages, and it is easy to imagine further adsorption, for instance, on a film of the complex (*a*). Such compounds might conceivably react with water and more oxygen (probably held in intimate contact) to form oxalic acid; also they contain the true peroxide structure and might be expected to react with dilute sulphuric acid to form hydrogen peroxide.

The author thanks Professor H. B. Baker, C.B.E., F.R.S., for his interest throughout the work and for his valuable suggestions.

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