Oxidations on Charcoal. By Miss W. M. WRIGHT. (Communicated by Mr E. K. RIDEAL.)

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It is well known that charcoal possesses catalytic properties. It accelerates the decomposition of hydrogen peroxide, the removal of bromine from $\beta\beta$-dibromo propionic acid and enables certain oxidations to take place in air at ordinary temperatures.

Warburg* studied the oxidation of oxalic- and of some α-amino-acids in dilute solution, in the presence of charcoal. He found that when he used blood charcoal, which contains iron, the reaction was inhibited by hydrocyanic acid in very low concentrations; if, however, he employed sugar charcoal, the rate of oxidation was not appreciably affected by small quantities of HCN. Sugar charcoal is itself slowly oxidised when it is suspended in water in contact with air. Warburg suggested that the catalytic action of blood charcoal was due to the iron, while the oxidation of acids by sugar charcoal was a coupled reaction with the auto-oxidation of the latter.

A more detailed investigation of oxidation at the surface of charcoals has now been made. The rate of oxidation was measured by a Barcroft differential manometer using 100 mgms. of charcoal in 3 c.c. of solution. In the first series of experiments Kahlbaum's sugar charcoal was used. It was previously activated by heating in silica vessels.

The rate of auto-oxidation was examined by shaking a suspension of the charcoal in conductivity water in a Barcroft adsorption vessel, in which the CO_2 evolved is adsorbed by a 40 per cent. solution of potash, so that the pressure change is proportional to the oxygen uptake. At 40°, the rate of oxygen uptake k is 0·13 mm.^{3} oxygen (N.T.P.) per milligram of charcoal per hour; at 50° the rate is 0·23. The temperature coefficient therefore is 1·80.

The reaction is of zero order, and independent of the pressure of the oxygen over the range examined. It therefore appears that the auto-oxidation takes place on very active parts of the charcoal surface, which are always saturated with oxygen; and the rate of reaction measured is equal to the rate of evaporation of carbon dioxide from them. Further, the combustion must proceed along a chain of carbon atoms, for, if it spread out on the surface in an expanding ring, the rate would continually increase, but this does not occur.

An attempt was made to measure the area of the auto-oxidisable surface by fractional poisoning with potassium ferricyanide, and with amyl alcohol.

* Warburg, *Pflüger's Arch.* vol. 55, p. 547 (1914).

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The minimum concentration of poison required to arrest completely the auto-oxidation of the charcoal was determined, and the number of molecules adsorbed per milligram of charcoal, obtained from the adsorption isotherm; assuming that each molecule is adsorbed on one carbon atom, this gives the number of auto-oxidisable atoms per milligram. The total number of atoms on the surface per milligram was calculated from the adsorption maximum of amyl alcohol. The results showed that not more than 0·38 per cent. of the charcoal surface is auto-oxidisable.

The oxidation of oxalic acid to carbon dioxide and water on the surface of sugar charcoal is not coupled with the auto-oxidation of the charcoal, for the latter can be completely inhibited by the addition of small quantities of amyl alcohol, without appreciably affecting the rate of oxidation of the acid.

Warburg* states that the oxidation velocity of oxalic acid varies inversely as its bulk concentration. By starting with very dilute solutions, however, it was found that with increasing concentration, the velocity rises rapidly to a maximum, and falls off again. The position of this maximum is not appreciably altered by a rise in temperature of 10°, the temperature coefficient being 2·0 for all concentrations observed.

The maximum velocity is identical in air and in oxygen, in the latter, however, it is displaced towards higher oxalic acid concentrations, showing that at the higher pressure the acid is displaced from the surface by the oxygen, and a stronger solution is required in order that the two constituents may again be present in the optimum proportions.

By fractional poisoning with amyl alcohol it was shown that not more than 40 per cent. of the surface is catalytically acitive.

With Merk's blood charcoal, the maximum oxidation velocity of oxalic acid is some fifteen times that obtained with sugar charcoal. The specific surface of the former, as determined by adsorption of methylene blue, is eight times that of the latter.

The rate of oxidation is retarded by the addition of amyl alcohol, and the degree of poisoning is proportional to the fraction of surface covered up to 80 per cent. poisoning. Complete poisoning could not be obtained, owing to the slight solubility of amyl alcohol. By extrapolation, the catalytically acitive surface was estimated as 60 per cent. of the total surface.

If potassium cyanide is used as a poison, and the degree of poisoning plotted against the fraction of surface covered, it is found the reaction velocity is reduced to one-half of its original value, when only 1·5 per cent. of the surface is covered with adsorbed cyanide. At this point there is a distinct break in the curve, further addition of cyanide producing relatively little increase in

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the amount of poisoning. At high concentrations there is an increase in the oxygen-uptake, owing to the oxidation of the KCN itself.

This shows that there are two catalytically active areas on blood charcoal, one small, highly active surface, which is preferentially poisoned by the cyanide ion, and another larger, less active surface. If the former is poisoned by the addition of $M/1000$ KCN, and the maximum velocity on the remaining surface determined, the specific activity of the two areas can be calculated.

The results show that the very active surface A oxidises $1{\cdot}1 \times 10^{12}$ mols oxalic acid per cm.^{2} surface per sec., while the active surface B oxidises $2{\cdot}8 \times 10^{10}$ mols oxalic acid per cm.^{2} surface per sec. The active surface of sugar charcoal oxidises $3{\cdot}6 \times 10^{10}$ mols per sec. The ratio of these activities $C:B:A$ is as $1{\cdot}3:1:39{\cdot}4$.

Since the poisons used are not absolutely selective, the areas measured represent the maximum active areas and therefore the activities calculated from these are only minimum values. Areas C and B are probably identical, and may be attributed to the carbon surface. Surface A, which is about forty times as active as the former, probably consists of an iron-carbon union.

The temperature coefficient of the oxidation of oxalic acid on blood charcoal is $k\,(50°)/k\,(40°) = 1{\cdot}80$; this represents the resultant of the action on the two surfaces.

By finding the temperature coefficient, when the iron-containing area is poisoned with potassium cyanide, and correcting for the slight decrease in adsorption of the acid at the higher temperature, the temperature coefficient for each surface can be obtained. This gives for

$$\text{surface } A,\ k\,(50°)/k\,(40°) = 1{\cdot}67,$$
$$\text{surface } B,\ k\,(50°)/k\,(40°) = 1{\cdot}93,$$
$$\text{surface } C,\ k\,(50°)/k\,(40°) = 2{\cdot}00.$$

From these values the heat of activation Q is found to be for

surface A, 10,240 calories
surface B, 12,940 ,,
surface C, 13,660 ,,

Warburg* claims that only nitrogenous charcoals can be activated by iron. To test this point, some nitrogen-free charcoals were prepared containing small quantities of iron salts, together with control charcoals made without the addition of iron. A mixture of sugar and ferric chloride in a little water was heated in an atmosphere of carbon dioxide, until carbonisation was complete.

* Warburg, *Biochem. Zeits.* vol. 145, p. 461 (1924).

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The resulting charcoal was baked out in a stream of hydrogen for six hours in order to remove the CO_2, and reduce the iron. The iron-containing charcoals were more active than the control specimens, and resembled blood charcoal, in that their catalytic activity was diminished by the addition of small quantities of potassium cyanide, and the specific activity of the two surfaces was of the same order in both charcoals.

Blood charcoal, surface A $= 3{\cdot}0 \times 10^{-5}$ c.c. O_2 per sq. cm.
Nitrogen-free charcoal, surface A' $= 4{\cdot}3 \times 10^{-5}$,, ,, ,,
Blood charcoal, surface B $= 7{\cdot}6 \times 10^{-7}$,, ,, ,,
Nitrogen-free charcoal, surface B' $= 9{\cdot}0 \times 10^{-7}$,, ,, ,,

Paneth and Radu's* data show that nitrogenous charcoals have a greater specific surface than those free from nitrogen; nitrogenous compounds appear to exert a peptising influence on the charcoal. This has now been shown by preparing a series of charcoals from mixtures of urea and sugar.

The specific surface of the charcoals increased with the urea content of the mixture up to about 5 per cent. urea, and the yield of active charcoal was greater than that obtained from sugar alone, for the nitrogenous charcoals are less easily oxidised, and thus there is less loss by combustion in the heating processes.

Percentage urea	Specific surface square metres per gram	Yield per 100 grams of sugar
0	22	8·0
0·5	42	9·8
5·0	84	12·2
10·0	83	15·0

Therefore, although iron can activate charcoal in the absence of nitrogen, yet nitrogenous charcoals are, in general, more efficient catalysts than pure sugar charcoals, owing to their greater specific surface; also, the ammonia produced during carbonisation of the former aids in reducing the iron; whereas the iron in sugar charcoal is inactive unless it is reduced in hydrogen. Further, some experiments now in progress indicate that an iron-carbon-nitrogen complex is a more active catalyst than the iron-carbon union.

In conclusion, I wish to thank Mr Rideal for suggesting this work, and for his interest and advice throughout its course.

* Paneth and Radu, *Ber.* vol. 57, p. 1221 (1924).

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