CCXL.—*Low Temperature Oxidation at Charcoal Surfaces. Part II. The Behaviour of Charcoal in the Presence of Promoters.*

By Eric Keightley Rideal and Winifred Mary Wright.

In a previous communication (J., 1925, **127**, 1347), it was shown that the surface of a pure sugar charcoal could be differentiated into areas having different properties. A small fraction of the surface (0·35%) was autoxidisable, whilst a portion (*ca.* 40·5%) was capable of catalysing the oxidation of certain organic acids such as oxalic acid; the remaining portion could adsorb this acid, but could not catalyse its oxidation. These three areas were likewise differentiated in their powers for adsorbing the poison employed, *viz.*, amyl alcohol. In addition, evidence was presented for the assumption that in such oxidative processes both oxygen and the organic acid were adsorbed on the active area. This view has since received confirmation by the work of Freundlich and Fischer (*Z. physikal. Chem.*, 1925, **114**, 413) on the catalytic oxidation of thiocarbamide. Warburg (*Biochem. Z.*, 1924, **145**, 461) was of the opinion that the catalytically active areas in charcoal consisted of iron–carbon–nitrogen complexes (designated for brevity Fe–C–N), neither carbon nor carbon admixed with iron possessing any sensible catalytic activity. Since it has been shown that nitrogen- and iron-free charcoal surfaces do, in effect, possess a well-defined catalytic activity, it seemed of importance to examine in some detail the specific effects of nitrogen and iron both separately and conjointly on the catalytic properties of charcoal.

The Effect of Nitrogen.

An inspection of the data of Paneth and Radu (*Ber.*, 1924, **57**, 1221) shows that charcoals prepared from nitrogenous sources possess, in general, greater specific surfaces than charcoals produced from nitrogen-free compounds such as sugar; thus, apart from any specific catalytic activity due to C–N complexes in the surface of such charcoals, it might be anticipated that the catalytic activity per g. of the former type of charcoal would be greater than that for a sugar charcoal, unless the fraction of the surface catalytically active was considerably less than the corresponding fraction (40·5%) for sugar charcoals.

Experiments with a number of nitrogenous organic compounds incorporated with sugar showed that a great extension of surface of the resultant charcoal could readily be obtained. Urea was found to be the simplest material which would give uniform results.

In the following table are given the specific surfaces, as determined by the saturation point with methylene-blue (compare Part I), for a number of charcoals prepared by carbonising sugar with the admixture of various quantities of urea under approximately identical conditions.

% Urea.	Specific surface in sq. m. per g.	Yield of charcoal per 100 g. of sugar.	% Urea.	Specific surface in sq. m. per g.	Yield of charcoal per 100 g. of sugar.
0	22	8·0	5·0	84	12·2
0	18	7·2	10·0	83	15·0
0·5	42	9·8	25·0	81	16·2
0·5	37	10·1			

The adsorptive capacities of charcoals are much improved by prolonged heating, during which process adsorbed hydrocarbons and part of the charcoal are burnt. Many charcoals employed for industrial purposes represent a residue of only some 7% of the original wood charcoal employed. The yield of urea-sugar charcoal is greater than that of ordinary sugar charcoal and in fact somewhat surpasses the best charcoals from technical sources examined by us. The determination of the specific areas for sugar charcoals and for 10% urea-sugar charcoals during this process of activation or slow and selective combustion gave the following results :

Sugar Charcoals.

	I.		II.			III.			IV.	
% Charcoal residue	100	25	100	63	34	100	32	24	100	34
Sq. metres per g.	21	85	26	46	180	27·6	191	200	25	120

Urea-sugar Charcoals.

	I.		II.			
% Charcoal residue...	100	25	100	45	30	22
Sq. metres per g. ...	81	244	80	182	194	190

It may be concluded that the incorporation of 10% of urea in sugar and activation of the resultant charcoal by slow combustion until some two-thirds have been removed by oxidation, will produce a charcoal of specific surface of 200 sq. m. per g. Similar effects can be obtained with benzoic acid as a source of the carbon.

The catalytic activity of a nitrogen-carbon charcoal for the oxidation of oxalic acid was determined by measurement of the oxygen consumption and carbon dioxide evolution in a Barcroft differential shaking manometer as described in Part I.

Since charcoals made from sugar always contain a small quantity of iron and other inorganic impurities, the pure nitrogen–carbon charcoal was prepared from a mixture of 30 g. of benzoic acid with 1 g. of urea. (The benzoic acid was purified by sublimation, and the urea as follows : 5 g. of urea were dissolved in water, together with 1 g. of aluminium chloride; the aluminium and any iron present were precipitated by addition of ammonia, the solution was filtered, and the filtrate evaporated on a water-bath until the urea began to crystallise.) The charcoal was obtained by dropping small quantities of the mixture into a red-hot platinum crucible. The charcoal was washed with iron-free hydrochloric acid, and then with water, dried, and finally heated in a closed platinum crucible for $\frac{1}{2}$ hour. Yield 2·5 g. The charcoal was almost ash-free: 0·5 g. was incinerated in a weighed crucible and no weighable residue could be detected, but a slight iron reaction was obtained on addition of potassium thiocyanate and acid to the crucible; there was not enough charcoal available for a quantitative determination of the iron, but it was probably less than 0·02%.

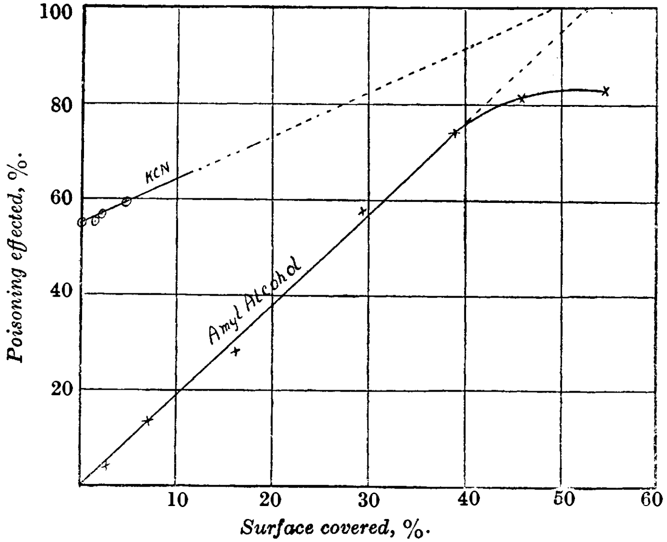
The nitrogen was estimated by Kjeldahl's method: 0·26 and 0·5 g. of charcoal yielded 2·12 and 2·22% N respectively; and the specific surface, as estimated by the adsorption of methylene-blue, was 87·5 sq. m. per g. The maximum velocity of oxidation of oxalic acid with this charcoal was obtained with a concentration of 0·012 mol. per litre and, at 40°, was 1·23 mm.^{3} of oxygen per mg. of charcoal per hour. Since the charcoal contained a small quantity of iron, it was decided to employ potassium cyanide in the preliminary experiments on poisoning. The adsorption isotherm of the cyanide in the presence of the oxalic acid (0·012 mol. per litre) and of hydrochloric acid equivalent to the cyanide employed was determined, the cyanide in solution being estimated both colorimetrically with iron salts and electrometrically with the aid of standard silver nitrate. In addition to potassium cyanide, amyl alcohol was used as a poison, the adsorption isotherm being determined with the aid of drop-weight measurements (compare Part I). The data obtained are shown in Fig. 1.

It is clear that potassium cyanide selectively poisons a patch which is not affected by amyl alcohol. Since the extent of this very active area is certainly less than 0·1% of the total area, and as Warburg (*loc. cit.*, Part I) has shown that cyanide sensitivity is determined to a great extent by the iron content of the charcoal, this very active area may be ascribed to the iron present as impurity. The velocity of oxidation after the poisoning of this area has fallen to 0·54—0·55 mm.^{3} of oxygen per mg. per hour, and this residual velocity must be attributed to the remaining C–C and N–C active surfaces. It is to be noted from the curves that the potassium cyanide poisoning curve is again linear after the abrupt break at the point where all the iron has been poisoned. Prolongation of the curve was rendered difficult by the autoxidation of this salt in concentrated solutions, in which a departure from the linear character of the curve is noticeable. A few of the determinations in such solutions were corrected for the autoxidation and the points so corrected were close to those anticipated from the experimental data for dilute solutions. The amyl alcohol poisoning curve, however, is directed towards a point which indicates that complete poisoning would be effected when *ca.* 52·4% of the surface is covered —a value to be compared with 40·5% in the case of pure sugar charcoal. These poisoning curves are both linear and thus we cannot differentiate, either with potassium cyanide or with amyl alcohol, between the C–C and the C–N complexes, if indeed such exist. Similar poisoning experiments with potassium thiocyanate, chloroform, aniline and acetone likewise failed to reveal any break in the curves. The activity per sq. cm. of active surface (excluding the small, highly active area which is sensitive to potassium cyanide and probably contains iron) is

FIG. 1.

Oxidation of 0·012 M-*oxalic acid.*

Poisoning of charcoal made from benzoic acid + urea.



$$\frac{0{\cdot}55 \times 100}{87{\cdot}5 \times 52{\cdot}4 \times 10^4} = 1{\cdot}26 \times 10^{-6} \text{ c.c. of oxygen per sq. cm. per hour.}$$

From the data in Part I the activity for nitrogen-free sugar charcoal was found to be 0·915 × 10^{-6} in the same units. It may be concluded that the specific activity as well as the adsorptive powers of the C–N complex do not differ from those of the active C–C surface, and that the incorporation of nitrogen in a charcoal with the aid of urea results in a large increase in total specific surface (26·6 to 87·5 sq. m. per g.), but does not affect the specific activity of the active surface, *i.e.*, the rate of oxidation per sq. cm. on the active surface under conditions of optimum velocity (0·915 and 1·26 × 10^{-6} c.c. of oxygen per sq. cm. per hour, respectively).

Promotion with Iron.

A solution of 48·5 g. of sugar and 1·5 g. of ferric chloride in a small quantity of water was evaporated to dryness in a silica crucible in a stream of carbon dioxide. The temperature was then raised until carbonisation was complete, and the charcoal maintained at a dull red heat for one hour. After baking in a stream of hydrogen, to remove the adsorbed carbon dioxide and reduce any iron which might be present in the oxidised form, the charcoal was cooled, extracted several times with hydrochloric acid and water, and dried by heating in hydrogen. 8 G. of charcoal were obtained. An iron-free charcoal was prepared by a similar method to serve as a control. The rates of oxidation of oxalic acid were determined with the two charcoals and well-defined maxima of the oxalic acid concentration–velocity curves were obtained as in the previous experiments (Part I).

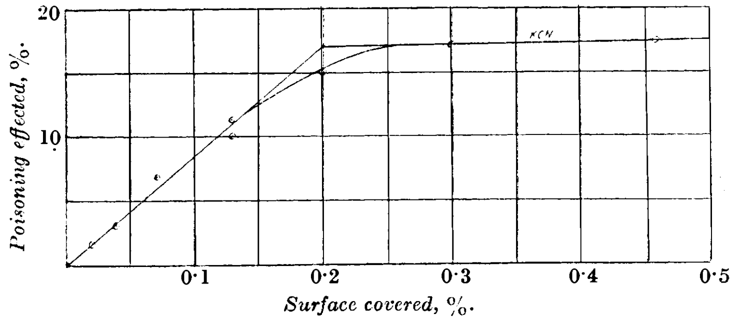
For the iron charcoal the maximum velocity occurred with 0·015 *M*-oxalic acid, and was 0·7 $mm.^3$ of oxygen per mg. of charcoal per hour. The control gave a velocity of 0·18 in the same units at a concentration of 0·01*M*-oxalic acid. The total surface as determined by adsorption of methylene-blue was 140 sq. m. per g. The iron charcoal was specifically poisoned by potassium cyanide, but the control was not affected by this salt in small concentrations. The adsorption isotherm of potassium cyanide in the presence of 0·015*M*-oxalic acid and hydrochloric acid in concentrations equivalent to the salt was determined. Then, assuming each cyanogen ion to be adsorbed on one carbon atom, the fractions of surface covered corresponding with different degrees of poisoning can be calculated. The data are presented in Fig. 2.

It will be seen that there is a marked break in the curve corresponding to 0·2% of the surface covered and 17% poisoning, showing that there is a small, highly active area very sensitive to the cyanide. Since this area does not occur with the control charcoal, it can reasonably be regarded as consisting of the Fe–C complex.

This very active area is likewise not revealed by poisoning with amyl alcohol. By extrapolation of the cyanide and amyl alcohol poisoning curves, it was found that the surface would be completely poisoned when 44% was covered. From these data, we can calculate the specific activities of the surfaces consisting of C–C and Fe–C complexes. The specific activity of the very active surface of area 140 × 0·2% = 0·28 sq. m. per g. with an oxygen consumption of 0·70 × 17% = 0·119 c.c. per g. per hour is $0{\cdot}119/2{\cdot}8 \times 10^{-3} = 42{\cdot}5 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour. The specific activity of the less active surface of area 140 × 44% = 61·6 sq. m. per g. with an oxygen consumption of 0·70 × 83% = 0·58 c.c. per g. per hour is $0{\cdot}812 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour—a value very similar to that obtained for the active surface of sugar charcoal ($0{\cdot}915 \times 10^{-6}$).

We may conclude that the Fe–C complex possesses a specific activity of $42{\cdot}5 \times 10^{-6}/0{\cdot}85 \times 10^{-6}$ or 50 times that of the ordinary active carbon surface.

FIG. 2.



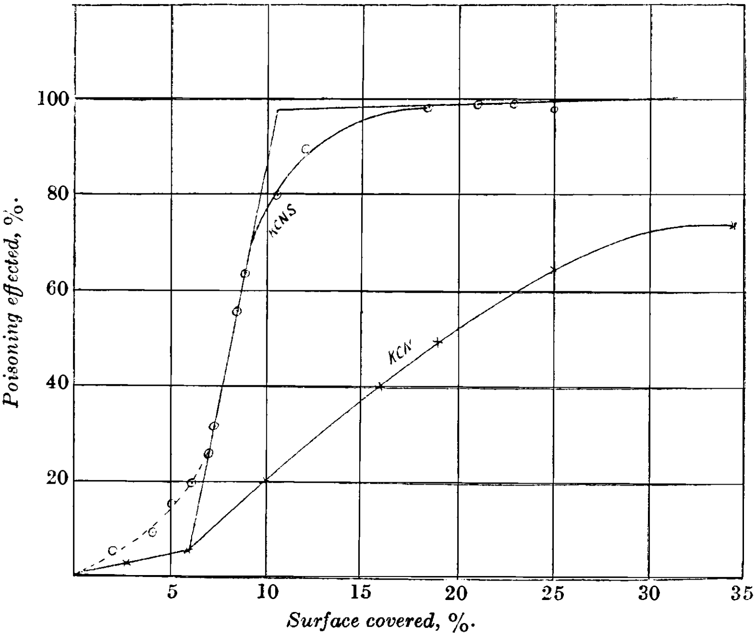
Promotion with Iron and Nitrogen.

The experiments already recorded indicate that in nitrogen–carbon charcoals, if there be any specific activity due to a C–N complex, it is not greatly different from that of the ordinary charcoal, the function of the nitrogenous constituent being mainly to increase the specific area or to "peptise" the carbon. In the case of the iron–carbon charcoals, on the other hand, very definite evidence is presented for the existence of a specific Fe–C complex which is some 50 times more active than ordinary carbon. We should anticipate that for the ternary system iron–carbon–nitrogen the following groupings might be present as complexes on the surface C–C, C–N, C–Fe, Fe–N, Fe–C–N. Since the first two cannot be distinguished in catalytic activity and since, in the presence of a large excess of carbon the complex Fe–N is not likely to be present (and, even if present, iron nitride possesses no catalytic activity), the number of active complexes is reduced to three, *viz.*, C–C, C–Fe, and Fe–C–N. The specific activities of the first two groups have already been determined, so we may reasonably assign any new specific activity of a third portion of such a complex charcoal to the Fe–C–N complex to which Warburg attributed all the catalytic activity.

The charcoal was prepared from mixtures of sugar, urea, and ferric chloride. The activities of the different areas on this charcoal were determined as before by fractional poisoning. The specific surface as determined by adsorption of methylene-blue was 29·8 sq. m. per g. It oxidised oxalic acid very rapidly, the maximum velocity occurring with an acid concentration of 0·015 mol. per litre; the oxygen consumption was 12 mm.^{3} per mg. of charcoal per hour. The curve obtained by poisoning with potassium cyanide was of a different nature from that obtained with nitrogen-free iron-containing charcoals. On plotting the degree of poisoning and the fraction of surface covered, an S-shaped curve was revealed, the two points of inflexion suggesting that there are three active areas on the charcoal. The upper part of the curve could not be obtained accurately owing to the oxidation of the potassium cyanide itself.

FIG. 3.

Fe-*urea sugar charcoal.*



When potassium thiocyanate was used as a poison, the form of the curve was similar to that obtained with the cyanide, but the middle portion was steeper and the points of inflexion were more marked. (Thiocyanate was apparently more truly selective in its action than cyanide on the Fe–C–N complex, but less selective on the Fe–C complex.) The activities of the different portions of the charcoal surface were calculated as before. The first area gave an activity of the same order as the iron area on nitrogen-free iron charcoal, the third area was of a similar activity to the surface of the sugar charcoal, whilst the second area was about 15 times as active as the Fe–C surface. With these two poisons the following data were obtained.

With KCNS.

Surface.	Area (sq. cm. per g.).	% Total surface.	% Total activity.	Activity mm.^{3} O_2 per mg. per hr.	Specific activity (c.c. O_2 per sq. cm. per hr.).
Fe–C	$1·8 \times 10^4$	6	13	1·57	87×10^{-6}
Fe–C–N	$1·35 \times 10^4$	4·5	86·65	10·4	770×10^{-6}
C–C	$6·0 \times 10^4$	20·0	0·35	0·035	$0·70 \times 10^{-6}$
		With KCN.			
Fe–C	$1·8 \times 10^4$	6·0	6·0	0·72	40×10^{-6}
Fe–C–N	$3·0 \times 10^4$	10·0	40·0	4·8	160×10^{-6}

The limitations of the method are apparent from the above data. It is clear that potassium cyanide is much more selective than potassium thiocyanate in its action on the Fe–C complex, *i.e.*, that it will completely poison the Fe–C area before affecting the Fe–C–N area to the extent that potassium thiocyanate does. From these and the foregoing data we may assign the following approximate ratios for the specific activities of the three areas C–C Fe–C, and Fe–C–N = 1 : 50 : 800. These ratios, however, must be regarded as mean values rather than absolute determinations, since, as has been indicated, we have definite evidence that cyanide and possibly thiocyanate are not completely selective in their actions.

It will be observed that not only is Warburg's contention of the great specific activity of the Fe–C–N complex completely substantiated by these data, but also that the other types of complexes present possess by no means negligible specific activities.

In addition, the peculiarities of the poisons employed present interesting features. Amyl alcohol does not distinguish between these patches of varying activity, but does differentiate between catalytically active and inactive carbon, *i.e.*, the length of life of the alcohol molecule on the active carbon must be greater than on the inactive portion and greater than that of oxalic acid on the active portion. Potassium cyanide and thiocyanate, on the other hand, are adsorbed much more readily on the Fe–C surface than on the Fe–C–N or the active carbon surfaces, but the difference in the lengths of life of the cyanide ion on the Fe–C and Fe–C–N surface is not so great as for the thiocyanate ion, which is accordingly more suitable as a selective poison. Whilst the residual affinity of the Fe–C complex for cyanide and thiocyanate is greater than that of the Fe–C–N complex, the catalytic activity for oxidation of oxalic acid is, on the other hand, much less. All poisons are thus not necessarily adsorbed preferentially on the most active catalytic patches, and in addition a simple equation for the adsorption isotherm on a solid surface of irregular structure does not obtain.

Summary.

The effect of nitrogen and iron on the catalytic behaviour of charcoal in the oxidation of oxalic acid has been examined in detail. It is shown that the incorporation of these " promoters " in the carbon results in an extension of the total surface and possibly a small extension in the fraction of the surface which is catalytically active. At the same time, two new types of catalytically active surface make their appearance : an iron-carbon-nitrogen complex surface with a specific activity some 800 times that of the original active-carbon surface, and an iron-carbon surface with a specific activity some 50 times that of the original surface.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

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