CCCCXXX.—*Low Temperature Oxidation at Charcoal Surfaces. Part III. The Behaviour of Blood Charcoal and the Influence of Temperature on the Reaction Rate.*

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In previous communications (J., 1925, **127**, 1347; this vol., p. 1813) it was shown that charcoals containing both iron and nitrogen were catalytically active for the oxidation of oxalic acid, and that the surface of the charcoal was by no means uniform but could, by the method of selective poisoning, be divided into areas of different specific catalytic activities. Reasons were given for the assumption that two of the areas of high catalytic activity were promoted areas, *i.e.*, characterised by their chemical composition; thus, the specific activity in the oxidation of oxalic acid of a surface of an iron–carbon–nitrogen complex was about 800 and that of an iron–carbon complex about 50 times that of the catalytically active portion of the charcoal.

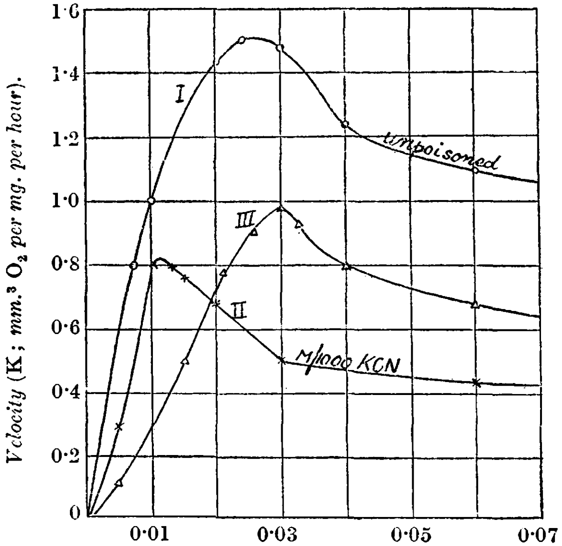
Since blood charcoal has been employed for a number of diverse purposes, it seemed desirable to examine this material by the method of selective poisoning and thus to ascertain the nature and extents of the patches of various specific activities.

EXPERIMENTAL.

Merck's blood charcoal was employed after purification by treatment with hydrochloric acid and heating for 2 hours in a silica crucible at low red heat. (Analysis showed Fe, 0·037; N, 7·0; and 0·80% of salts of calcium and sodium.) Its specific surface was found, by the saturation method with methylene-blue, to be 210 sq. m. per g.—some eight times that of the pure sugar charcoal previously investigated. The rates of autoxidation and of oxidation of oxalic acid of various concentrations in the presence of poisons such as amyl alcohol and acidic potassium cyanide were studied with the aid of a Barcroft differential shaking manometer as described in Parts I and II. In every case, 100 mg. of charcoal were allowed to come to equilibrium with the oxalic acid solutions of various concentrations by agitation and separation in a centrifuge. To these solutions known amounts of amyl alcohol were added, the solutions agitated in the differential manometer, and the rate of oxygen uptake measured. The bulk concentration of the alcohol was measured by the drop-weight method, and hence the amount adsorbed was calculated.

FIG. 1.

Blood charcoal.



Conc. of oxalic acid (mol. per litre).

The autoxidisable area of blood charcoal was almost inappreciable and, although varying from sample to sample, did not exceed in any one case 0·03% of the total surface, the average rate of oxygen uptake at 40° being 0·008 mm.^{3} per mg. per hour. The maximum rate of oxidation of oxalic acid occurred in 0·025*M*-solution, as is evident from Curve I (Fig. 1).

On poisoning with amyl alcohol, a linear curve (see Fig. 2) was obtained up to 80% inhibition, beyond which no further poisoning occurred owing to limitations imposed by the sparing solubility of the alcohol. By extrapolation in the manner already described (Part I), the fraction of the total surface catalytically active was found to be 55%, a value to be compared with the following : sugar charcoal 40·5%, nitrogen–sugar charcoal 52%, iron–sugar charcoal 44%, iron–carbon–nitrogen charcoal 30%.* Blood charcoal thus possesses a relatively large specific surface, and a large fraction of the total surface is capable of catalytically accelerating the oxidation of oxalic acid.

The poisoning with cyanide was determined as follows : In each experiment a suspension of 100 mg. of charcoal in 0·02M-oxalic acid was employed and various concentrations of potassium cyanide with an equivalent of hydrochloric acid were added. The adsorption of the cyanide was determined from the bulk concentration at equilibrium as estimated by silver titration employing the electrometric method. The rate of oxygen uptake and its diminution with the increase in surface covered by the cyanide were determined with the aid of the differential manometer.

FIG. 2.

Blood charcoal and oxalic acid.

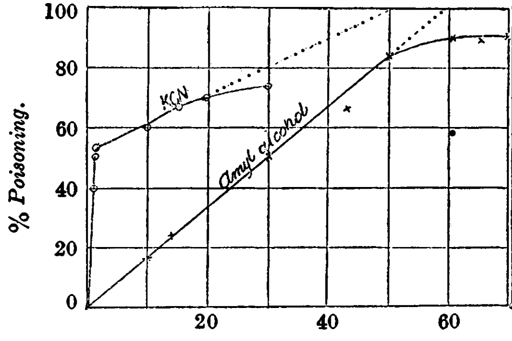
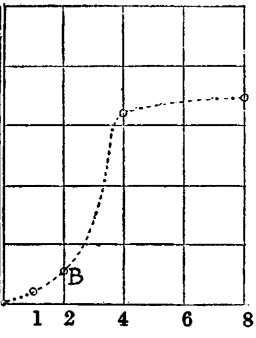


FIG. 3.



Only one well-defined break in the surface covered–velocity curve was obtained (Fig. 2). The marked break in the curve occurs at a point where only 1·2% of the total surface is covered, and thus 1·2% of the total surface is responsible for 54% of the total catalytic activity of the charcoal. This very active portion was poisoned

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* Kubota and Yoshikawa (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 223) have shown that a reduced-nickel catalyst has three distinct catalytically active areas each of which can be completely and selectively poisoned. Although the total area may vary with the mode of treatment of the catalyst, they claim that the ratios of the areas remain unchanged. A critical examination of their data, however, does not lead us to an unqualified acceptance of this view.

by $M/1000$-potassium cyanide and the maximum velocity of oxygen uptake on the remainder of the charcoal occurred with an oxalic acid concentration of $0{\cdot}01M$ (Curve II, Fig. 1) comparable with that for sugar charcoal, *i.e.*, $0{\cdot}0075M$. At this concentration the reaction velocity was $k = 0{\cdot}81$ mm.^{3} of oxygen per mg. of charcoal per hour. From the velocity–concentration curves for the unpoisoned and the partially poisoned charcoal the reaction velocity maximum (see Curve III, Fig. 1) for the more active surface was found to be $k = 0{\cdot}98$ mm.^{3} of oxygen per mg. per hour. Since the total surface of the charcoal is 210 sq. m. per g. and 1·2% of this is the very active iron–carbon surface, the specific activity of this surface is accordingly $0{\cdot}98/(210 \times 10^4 \times 0{\cdot}012) = 39 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour. In a similar manner, the specific activity of the less active area is found to be $0{\cdot}76 \times 10^{-6}$ in the same units. When these values are compared with the specific activities of the three active patches obtained in the synthetic charcoals (for the C–C, $k = 0{\cdot}70 \times 10^{-6}$; for the Fe–C, $k = 40 \times 10^{-6}$; and for the Fe–C–N, $k = 770 \times 10^{-6}$), it would appear that blood charcoal contains but two active patches—one of 1·2% of the total area possessing an activity comparable with that of the synthetic Fe–C complex, and the other corresponding to unpromoted active carbon. It is somewhat remarkable that no sign of an iron–nitrogen–carbon complex is observed in the curves in spite of the fact that this charcoal contains not less than 7% of nitrogen.

The Range of Influence of the Iron Promoter.—The dispersion of the iron in the blood charcoal must be fairly uniform and we may regard the charcoal as an intimate mixture of carbon and iron atoms in the ratio of 12,000 : 1. With such a bulk distribution the surface distribution will be of the order of $(12{,}000)^{2/3} : 1$ or 536 : 1. On the assumption that every iron atom in the surface is active in promotion, and since the active area is 1·2% of the total surface, one atom of iron renders $536 \times 1{\cdot}2/100 = 6{\cdot}4$ (or, say, 6) atoms of carbon active, both for the selective adsorption of cyanides and for the catalytic oxidation of oxalic acid. The existence of an iron atom in the centre of a benzene ring or with six co-ordinated carbon atoms, comparable with its complex cyanide ions, would offer a simple interpretation of this remarkable result.

Attempts to achieve such a high carbon : iron ratio for the active patches in synthetic charcoals did not succeed, and it appeared likely that uniform dispersion of the iron could not be readily obtained when incorporated as a simple iron salt in a mixture undergoing carbonisation.

The Temperature Coefficients of the Reactions on the Active Surfaces.

In homogeneous gas reactions it is possible to calculate the energy of activation from the temperature coefficient. Certain limitations are imposed in dealing with heterogeneous actions. Before such calculations can be made it is necessary to be certain that we are dealing with identical concentrations of the reactant over the temperature range examined. In the case under consideration, this involves the assumption that the areas and natures of the active patches, as well as the adsorption of the reactants, remain unchanged or, if any changes occur, that these can be determined so that the necessary corrections can be applied.

Sugar Charcoal.—In Part I the temperature coefficient of the autoxidation of sugar charcoal was found to be $k_{50}/k_{40} = 1{\cdot}80$, and the reaction was independent of the oxygen pressure over wide ranges. On the assumption that the area and nature of an active patch over the temperature range examined remain constant, the concentration of reacting adsorbed oxygen–carbon complex is likewise constant, and the temperature coefficient can thus be utilised for determination of the energy of activation. By application of the Arrhenius equation $\log_e k_{50}/k_{40} = -E(1/T_2 - 1/T_1)/R$ we obtain a value of $E = 11{,}800$ cals. for the energy of activation for autoxidation. In the oxidation of oxalic acid both reactants are adsorbed; thus on either side of the point of maximum velocity the reactant adsorbed in excess acts as an inhibitor to the reaction. The temperature coefficient will therefore vary with the concentration of oxalic acid. The coefficient of adsorption of oxalic acid within the temperature range 30—40° is small and negative, being $3{\cdot}74 \times 10^{-7}$ mol. per mg. at 30° and $3{\cdot}70 \times 10^{-7}$ at 40°; that for the oxygen is unknown, although the solubility in the liquid falls from 0·0267 to 0·0233. We should anticipate that the temperature coefficient would steadily rise as we increase the oxalic acid concentration. This anticipation is verified by the following figures.

k_{40}/k_{30}	2·00	2·03	2·06
Molarity of oxalic acid	0·005	0·01 (optimum)	0·1

The correction to be applied for the change in adsorption with change in temperature thus appears to be relatively small, and on the assumption that the extent and nature of the active area remain unchanged we may determine the energy of activation for the sugar-charcoal complex from the temperature coefficient at the optimum, *viz.*, 2·03. This yields a value of $E = 14{,}020$ cals. per g.-mol. The validity of this value is based upon the hypothesis that oxalic acid and oxygen are both actually adsorbed on the active area. That oxalic acid is adsorbed could be demonstrated by the fact that on poisoning with amyl alcohol oxalic acid is displaced from the surface. In each experiment 100 mg. of charcoal were shaken with 10 c.c. of oxalic acid solutions of various concentrations. When adsorptive equilibrium was attained, the oxalic acid in solution was determined by titration with permanganate. Sufficient amyl alcohol was added to arrest catalytic oxidation and the bulk concentration of oxalic acid was again determined; calculation then gave the amount of acid displaced by the alcohol from the active patch, of which the area was 34·5% of the total area of 10·8 sq. m. per g., as determined by the methylene-blue method. The following table shows the results, from which it will be seen that oxalic acid is preferentially adsorbed on the catalytically active area, but even before the maximum velocity is attained this solute is likewise partly adsorbed on the inactive area.

Bulk conc. of oxalic acid.	Quantity adsorbed (g.-mols. per mg.) $\times 10^7$.	Quantity displaced by amyl alcohol on poisoning (g.-mols. per mg.) $\times 10^7$.	Quantity left on inactive portion (g.-mols. per mg.) $\times 10^7$.
0·0025*M*	0·5	0·5	0
0·005*M*	0·92	0·91	0·01
0·01*M* (optimum rate)	1·45	1·1	0·35
0·02*M*	2·1	1·8	0·30
0·04*M*	3·8	2·6	1·2

Blood Charcoal.—At the maximum (Curve I, Fig. 1) with 0·025*M*-oxalic acid the temperature coefficient was $k_{40}/k_{30} = 1·97$ (mean of six determinations). When the charcoal was poisoned by the addition of *M*/1000-potassium cyanide, the velocity at the new maximum at 0·01*M* (Curve II, Fig. 1) was 54% of its original value. The addition of *M*/500- and *M*/200-potassium cyanide did not reduce this velocity appreciably. It may therefore be assumed that 46% of the velocity is due to the iron-containing area. The temperature coefficient of this partially poisoned charcoal was 2·01, comparable with the value 2·03 found for the sugar charcoal.

If x be the coefficient of the iron-containing area, we thus obtain $2·01 \times 0·54 + 0·46x = 1·97$, whence $x = 1·92$. This is appreciably smaller than the temperature coefficient for the unpromoted area (2·03), and the corresponding value for the energy of activation is 12,900 cals.

A few experiments were likewise carried out with a charcoal prepared from Bismarck brown containing iron impurities (see Warburg, *Biochem. Z.*, 1924, **165**, 461). It resembled that prepared from urea, sugar, and ferric chloride in its high velocity of oxidation of oxalic acid and in its behaviour towards the poisons, cyanides and thiocyanates; it may therefore be assumed that it contains the three groups C–C, Fe–C, and Fe–C–N. The temperature coefficient of the unpoisoned charcoal at the maximum was 1·91. On the addition of potassium thiocyanate the velocity fell, and the temperature coefficient rose as follows :

Conc. of KCNS.	k_{40}.	% Poisoning.	k_{40}/k_{30}.
0	6·60	0	1·91
$M/10,000$	6·28	4·9	1·91
$M/5,000$	5·94	10·0	1·92
$M/2,500$	2·34	64·5	1·93
$M/1,250$	2·03	69·3	1·94

Sufficient charcoal was not available to determine the adsorption of the thiocyanate. As a rough approximation, the curve obtained by plotting bulk concentration against percentage poisoning (Fig. 3) suggests that there are three areas on this charcoal corresponding to those on urea–iron–sugar charcoal, and that about 15% of total activity is due to the Fe–C, 55% to the Fe–C–N, and 30% to the C–C areas (compare Part II). Then, substituting the values already obtained for the temperature coefficients for the C–C and Fe–C areas, that for Fe–C–N (X) is given by the equation $1{\cdot}92 \times 0{\cdot}15 + X \times 0{\cdot}55 + 2{\cdot}03 \times 0{\cdot}30 = 1{\cdot}92$, or $X = 1{\cdot}86$. This value can be confirmed more directly by the following method. Taking the point B (Fig. 3) of the partially poisoned charcoal, then, of the remaining activity, 65% is due to the Fe–C–N area and 35% to the C–C area; hence $0{\cdot}65X + 2{\cdot}03 \times 0{\cdot}35 = 1{\cdot}91$, or $X = 1{\cdot}86$. Taking X as 1·86, the energy of activation $E = 12{,}290$ cals.

We thus obtain for the energies of activation as determined from the temperature coefficients within the range 30—40°, for the C–C complex, 14,020; for the Fe–C complex, 12,900; and for the Fe–C–N complex, 12,290 cals. Whilst these critical increments are in the order anticipated inasmuch as the velocity of oxidation per sq. cm. rises with falling critical increment, yet they do not show the exponential relationship to the reaction velocities which is to be anticipated if the actual surface concentrations and arrangements of the molecules are identical, and if the complexes thus formed differ only in stability as was originally indicated (Part I).

It is probable that the nature of the surface adsorption of the oxygen is more important than the surface concentration of the oxalic acid; for, on comparison of the properties of the corresponding active areas (C–C) of sugar and blood charcoal, we find that, whereas they yield identical velocities for the oxidation of oxalic acid at the optimum concentrations (0·70 and $0{\cdot}76 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour) and almost identical temperature coefficients ($k_{40}/k_{30} = 2{\cdot}01$ and $2{\cdot}03$), yet the adsorption of oxalic acid differs markedly on the two surfaces.

The differences in the adsorbing properties of the catalytically active charcoal areas of blood charcoal and pure sugar charcoal may be tabulated thus :

	Charcoal.	
	Blood.	Sugar.
Conc. of oxalic acid for optimum rate	0·025*M*	0·01*M*
Adsorption of oxalic acid per sq. cm. of active area at optimum conc. (molecules)	$3{\cdot}12 \times 10^{14}$	$17{\cdot}9 \times 10^{14}$
Conc. of amyl alcohol to effect poisoning	0·023*M*	0·007*M*
Adsorption of amyl alcohol per mg. (g.-mol.)	$4{\cdot}22 \times 10^{-7}$	$1{\cdot}58 \times 10^{-7}$
Adsorption of amyl alcohol per sq. cm. of total surface	$1{\cdot}27 \times 10^{14}$	$8{\cdot}9 \times 10^{14}$
Adsorption of amyl alcohol per sq. cm. of active surface	$23{\cdot}3 \times 10^{14}$	$23{\cdot}3 \times 10^{14}$

Although these actual concentrations are based upon the hypothesis that one amyl alcohol molecule is attached to one carbon atom, a view which is open to criticism, yet the differences in the relative adsorptions indicate clearly that the two areas are not identical in all respects. These data incline us to the view that the process of the chemical reaction involves activation of the oxygen rather than of the acid. The catalytically active area is thus that portion of the charcoal surface which permits of excitation of adsorbed oxygen to a level at which it can react with oxalic acid. It seems probable that the area of a carbon surface which is catalytically active will vary with the nature of the substance undergoing oxidation; substances not readily oxidised may only undergo oxidation on a very restricted area on which the oxygen can readily be excited or activated to a relatively high potential. Such substances, which hitherto we have found to be characterised only by the possession of two polar groups, may also be defined by possessing different oxidation potentials, all of which are, however, below a certain critical value as determined by their powers of anodic depolarisation. We hope to inquire into the relationship between the rates of oxidation of such substances, the areas available for such oxidations, and the powers of anodic depolarisation which these substances may possess.

Summary.

The natures of the surfaces of blood charcoal have been examined by the methods previously detailed (J., 1925, **127**, 1347; this vol., p. 1813). Only two active areas were identified—one corresponding to the Fe–C complex, and one to the C–C complex of synthetic charcoals.

The area of carbon surface active for the oxidation of oxalic acid varies within the limits 30—55% of the total, depending on the method of preparation of the charcoal. The range of promoter action of one iron atom is found to extend to not more than six carbon atoms, and an analogy is sought in the complex iron cyanides.

The temperature coefficients of autoxidation and of oxidation of oxalic acid on the various active patches are determined. It is shown that the variation in adsorption of oxalic acid with the temperature is small; the variation in the temperature coefficient of oxidation with the concentration of oxalic acid is shown to follow the course anticipated. The distribution of oxalic acid between the active and inactive areas for various concentrations is determined. From the temperature coefficients, the following critical energy increments per g.-mol. are calculated : for autoxidation, 11,800 cals.; for oxidation of oxalic acid on the C–C complex, 14,020 cals.; on the Fe–C complex, 12,900 cals.; and on the Fe–C–N complex, 12,290 cals.

Whilst corresponding surfaces on a sugar and blood charcoal are identical in respect of the rates of oxidation of oxalic acid and the temperature coefficients of the rates, yet they differ in the amount of oxalic acid adsorbed per sq. cm. at the concentrations of maximum velocity. Stress is laid upon the importance of investigating the properties of adsorbed oxygen in more detail, and a relationship is suggested between the area of surface catalytically active, the velocity, and the depolarising potential of the substance undergoing oxidation.

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