CCCX.—*Low-temperature Oxidation at Charcoal Surfaces. Part IV. The Active Areas for Different Acids and their Relative Rates of Oxidation.*

By WINIFRED MARY WRIGHT.

IN previous communications (J., 1925, **127**, 1347; 1926, 1813, 3182), it was demonstrated that the surfaces of charcoals containing both iron and nitrogen could be differentiated by the method of selective poisoning into areas of different catalytic activities for the oxidation of oxalic acid. Whilst it was shown that these areas were differentiated in respect of their structure (the Fe–C–N, Fe–C, and C–C areas), of the rates of oxidation, and of the temperature coefficients of the oxidation processes on the areas, the method of estimating the total active carbon area from the amount of amyl alcohol absorbed only gave a maximum value for the fraction of the surface which was active. It is unlikely that the amyl alcohol is adsorbed preferentially only on the most active area if this is already covered with oxalic acid. It is also improbable that one amyl alcohol molecule is attached to but one carbon atom of the underlying surface. Since the active carbon area, even in very active promoted charcoals, greatly exceeds the more active areas of the promoted iron and iron–nitrogen patches, it was suggested by Dr. E. K. Rideal that it might be possible to determine both the adsorption of the poison and the displacement of the acid effected on this area.

Two specimens of charcoal were employed, Merck's blood- and Kahlbaum's sugar-charcoal; each charcoal was powdered to pass an 80-mesh sieve and heated for 2 hours at a low red heat in silica crucibles before use. The amyl alcohol content of the aqueous oxalic acid–amyl alcohol solutions employed was determined by the drop-weight method, and the oxalic acid content by titration with permanganate as previously described. The results obtained are shown in Table I.

TABLE I.

A. Merck's Blood-charcoal.

Oxalic acid.			Amyl alcohol.		
Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Displaced (g.-mol. per g.).	Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Mols. of alcohol required to displace 1 mol. oxalic acid.
0·025	$6\cdot93 \times 10^{-4}$	0	0	0	0
,,	5·76 ,,	$1\cdot17 \times 10^{-4}$	0·0156	$7\cdot31 \times 10^{-4}$	6·3
,,	4·58 ,,	2·35 ,,	0·0313	14·35 ,,	6·1
,,	2·20 ,,	4·73 ,,	0·0625	26·5 ,,	5·5
,,	0·0 ,,	6·93 ,,	0·125	49·0 ,,	(7·1)
0·5	$42\cdot0 \times 10^{-4}$	0	0	0	0
,,	38·3 ,,	3·7 ,,	0·05	24·5 ,,	6·6
,,	34·0 ,,	8·0 ,,	0·15	48·3 ,,	6·0
,,	30·1 ,,	11·9 ,,	0·25	69·5 ,,	5·8
0·75	50·0 ,,	0	0	0	0
,,	36·0 ,,	14·0 ,,	0·25	67·0 ,,	4·8
B.* Kahlbaum's Sugar-charcoal.					
0·75	$36\cdot9 \times 10^{-4}$	0	0	0	0
,,	33·9 ,,	$3\cdot0 \times 10^{-4}$	0·05	10×10^{-4}	3·3
,,	27·4 ,,	9·5 ,,	0·15	26 ,,	2·7
,,	14·9 ,,	22·0 ,,	0·25	40 ,,	1·8

* This was a hard brittle charcoal (unlike the soft charcoal used in Part I of this series).

It is clear from these data that the amyl alcohol is by no means preferentially adsorbed in the presence of oxalic acid, but that the number of mols. of amyl alcohol required to desorb one mol. of oxalic acid depends both on the relative concentrations of the two adsorbents and on the nature of the adsorbate. Since with blood-charcoal, at the concentration ($0\cdot025M$) giving the maximum oxidation velocity, 6 mols. of the alcohol only displace 1 mol. of the acid, the adsorption of the former does not give a trustworthy means of estimating the active area.

A search for a more efficient poison was made. Saturated solutions of diphenyl ether, *tert.*-butyl *p*-aminobenzoate, allyl *p*-aminobenzoate, octadecyl acetate, and hexadecylcarbamide were tried, but none of these reduced the rate of oxidation of oxalic acid by more than 70%. Solutions of dibromoacetic acid, ethylene dibromide, saponin, and sodium palmitate were also used; of these the soap was most efficient, giving 75% poisoning, but owing to its colloidal nature it was unsuitable for estimating the active areas. Ethylene dibromide, though very slightly soluble, gave 50% poisoning. A saturated solution of ethylene dibromide in aqueous ethyl alcohol (4% alcohol) gave 93% poisoning with oxalic acid, but further addition of alcohol gave an increased oxygen-uptake, owing to some secondary effect. A few determinations of displacement of oxalic acid by this substance were made, and from the degree of poisoning the active areas were calculated, but these results are untrustworthy owing to the unknown effect of alcohol on the oxidation velocity.

An attempt was made to poison the charcoal for the oxidation of M-formic acid by the addition of salts. Silver nitrate, copper sulphate, and aluminium chloride in $N/100$- and $N/10$-solutions were tried, but none of these gave more than 15% poisoning.

Finally, a saturated solution of caproic acid ($0{\cdot}046N$) was found to be a fairly effective poison of the charcoal for the acids investigated. Its absorption was determined by the drop-weight method.

The results of poisoning Kahlbaum's sugar-charcoal with caproic acid for the oxidation of four acids are given in Table II. [Contrary to our previous results (Part I, p. 1353), we find that formic acid is readily oxidised in the absence of impurities.]

Caproic acid is clearly a more selective poison than any material hitherto examined. We note that 2 mols. of both aminoacetic acid and formic acid, 1·5 mols. of malonic acid, and 1 mol. of oxalic acid are displaced on the adsorption of 1 mol. of caproic acid, from which we may deduce the relative areas of these molecules on adsorption. These small values are somewhat surprising, if, as is frequently assumed to be the case, caproic acid is adsorbed with its chain parallel or attached to the underlying carbon atoms. It appears that 1 mol. of caproic acid can displace only two carboxyl groups (compare formic, aminoacetic, and oxalic acids). In every case, complete poisoning would be obtained when $3{\cdot}1 \times 10^{-4}$ g.-mol. (mean value of A) of caproic acid is adsorbed per g. of charcoal.

The total carbon area active for oxidation is thus identical for all the four acids investigated on this particular charcoal, whilst the rates of oxidation of the various acids at their respective maxima

TABLE II.

Acid.	M.	$X \times 10^4$.	k.	P.	$d \times 10^4$.	$a \times 10^4$.	d/a.	$D \times 10^4$.	$A \times 10^4$.
Oxalic	0·015	4·5	0·75	62	2·1	2·0	1·05	3·4	3·2
,,	,,	,,	,,	91	3·2	3·1	1·03	3·5	3·4
Formic	0·5	6·2	0·55	11	0·6	0·4	1·5	5·4	3·6
,, ...	,,	,,	,,	69	4·1	2·05	2·0	6·0	2·9
Malonic	0·05	7·6	0·43	48	2·1	1·3	1·6	4·4	2·7
,, ...	,,	,,	,,	70	3·2	2·0	1·6	4·6	2·9
Aminoacetic	0·50	6·8	0·22	37	2·1	1·1	1·9	5·9	3·0
,,	,,	,,	,,	88	5·4	2·6	2·1	6·1	3·0
Oxalic *	0·015	4·5	0·75	95	1·33			1·4	
Formic * ...	0·5	6·2	0·55	93	3·0			3·25	

M = Concentration for maximum rate of oxidation (g.-mol. per litre).
X = Acid adsorbed on unpoisoned charcoal (g.-mol. per g. of charcoal).
k = Reaction velocity on ,, ,, (c.c. O_2 per g. of C per hr.).
P = % Poisoning.
d = Acid displaced for P % poisoning (g.-mols. per g. of C).
a = Caproic acid adsorbed for P % poisoning (g.-mols. per g. of C).
D = Acid displaced for complete poisoning (g.-mols. per g. of C).
A = Caproic adsorbed ,, ,, ,, (,, ,, ,,).

(D and A are calculated on the assumption that the degree of poisoning is proportional to the amount of acid displaced, or of poison adsorbed, although the results show that this is not strictly accurate.)

* These were poisoned with saturated ethylene dibromide in 4% aqueous alcohol. Malonic and aminoacetic acids were not poisoned readily by this substance.

are by no means identical. We may attempt a revaluation of the active area per g. of charcoal from these data. The total specific area of the charcoal, as determined by the saturation point of methylene-blue (see Part I), is 185 sq. m. per g. Since there is some doubt as to whether the methylene-blue method actually gives the total area, owing to the inability of the large molecules of the dyestuff to penetrate into the micropores of the charcoal, the surface saturation point of oxalic acid was determined from the adsorption isotherm.

From Table I, it is noted that 37×10^{-4} g.-mol. is adsorbed per g. from a $0{\cdot}75M$-solution; the adsorption isotherm is inconveniently flat near the maximum, but we may assume the maximum to be at *ca.* 40×10^{-4} g.-mol. per g.

The area of the adsorbed oxalic acid molecule is unknown, but, regarding it as equal to that of two expanded carboxyl groups, we obtain 50 Å. per mol., giving an area of 1212 sq. m. per g., or some seven times greater than that given by the methylene-blue method. The amount of oxalic acid displaced on complete poisoning by caproic acid is $3{\cdot}5 \times 10^{-4}$ g.-mol. per g., or 8·75% of the total surface is effective; on poisoning with ethylene dibromide, 1·4 × 10^{-4} g.-mol. per g. is displaced, or 3·5% of the total surface is effective, when the oxalic acid is employed as a means of evaluating the total area. These values are considerably smaller than those given previously where methylene-blue was employed. They are probably more accurate, in that the amount of poison adsorbed agrees closely with the amount of acid displaced, the poison being very much more preferential in its action than amyl alcohol.

Experiments with Promoted Charcoal.—An active promoted charcoal was prepared from sugar, carbamide, and ferric chloride, and the rates of oxidation of the four acids were determined on specimens of this charcoal. The oxidations due to the presence of the Fe–C–N and Fe–C areas were determined in the manner previously described by poisoning with solutions of potassium thiocyanate and potassium cyanide. The relative rates of oxidation of the four acids on the unpoisoned promoted charcoal are:

Acid.	C.c. of O_2 per g. per hr.	Relative rate.	Relative rate on sugar-charcoal.
Aminoacetic	1·2	1	1
Malonic	0·74	0·6	2
Formic	4·4	3·6	2·5
Oxalic	5·3	4·4	3·4

It will be noted that malonic acid is oxidised relatively slowly on the promoted charcoal. It was found also that there was no appreciable alteration in its rate of oxidation on the addition of either potassium cyanide or potassium thiocyanate, an indication that the promoted areas in the charcoal are not effective in oxidising this acid. The final product of oxidation of malonic acid (see Part I) is glyoxylic acid, and it is probable that hydroxymalonic acid is formed as an intermediate oxidation product. This hydroxy-acid may poison the iron in the presence of oxygen by the formation of a complex similar to that formed by ferrous salts with hydrogen peroxide in Fenton's test for hydroxy-acids. The transient purple of this test can indeed be obtained on application of Fenton's reagents to a solution of malonic acid which has been agitated with charcoal in the air for some hours. The two breaks in the velocity–poisoning curves indicative of the presence of two promoted areas (compare Pt. III) could be obtained with both aminoacetic and formic acids, and show that these acids, like oxalic acid, oxidise at different speeds on the three types of surface (the Fe–C–N, Fe–C, and C–C areas) present in the charcoal.

It was found difficult to obtain accurate values for the effective areas of these promoted areas for formic and aminoacetic acids, since the iron is slowly extracted from the charcoal in the presence of these acids. The approximate values are given in the following table :

Acid.	Velocity (c.c. of O_2 per g. per hr.) on Fe–C–N area.	Fe–C area.
Aminoacetic	1·08	0·009
Formic	3·90	0·042
Oxalic	4·37	0·049

The relative areas were found to be 9·1 sq. m. per g. for the Fe–C area and 5·5 sq. m. per g. for the Fe–C–N area. It will be noted that the relative rates of oxidation for the acids on the promoted Fe–C–N area are not widely different from those on the sugar-charcoal, and although the experimental error is much greater on account of the small velocities observed, a similar sequence in velocities is noted on the Fe–C area. We may conclude that the active patches on such charcoals are definite in extent and possess the property of oxidising a number of different acids, and that the difference in speed of reaction for different acids is to be attributed to the ease of reaction of the acid with the excited oxygen. This is probably present on the surface of the charcoal in the form of a peroxide which may be desorbed from the surface by excess of acid.

That the ease of oxidation of these fatty acids in aqueous solution follows the same sequence as the reaction velocity of catalytic oxidation at charcoal surfaces was demonstrated by measuring the depolarising capacity of solutions of these acids. These were determined by electrolysis between a small platinum cathode and a large, smooth platinum anode of an $N/5$-solution of sulphuric acid which was also N with respect to the acid under investigation. With the aid of a normal calomel electrode, salt junction, and Wheatstone bridge, the anode potential could be determined for various current densities at 25°. The curves obtained for the various acids are depicted in the figure.

It will be seen that neither acetic nor succinic acid exerts any appreciable depolarising action on the anodic evolution of oxygen, and neither of these acids is oxidised at observable rates with the charcoals hitherto examined by us ; on the other hand, the depolarising powers of oxalic, formic, and aminoacetic acids fall in the order of their rates of oxidation on charcoal surfaces. Tyrosine, a substance readily oxidised at charcoal surfaces, is included for comparison.

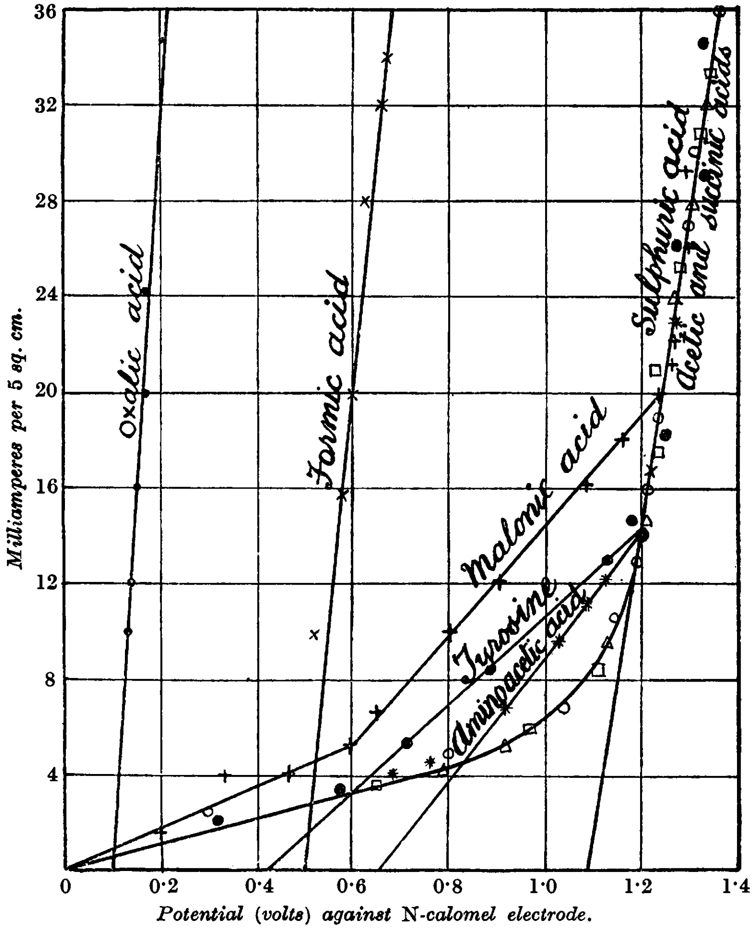
Summary.

The oxidation rates and the effects of poisoning with caproic acid on charcoal surfaces have been examined for formic, oxalic, malonic, and aminoacetic acids. It is found that the amounts

of poison absorbed required to inhibit the oxidation of these acids are identical. The effective catalytic area is found by this method to be about 4—8% of the total surface. With the exception of

Fig. 1.

Electrolytic oxidation of acids on a platinum anode (21 *sq. cm. area*).



N/5-H_2SO_4 ○. *N*/5-H_2SO_4 + *N* acetic acid □. *N*/5-H_2SO_4 + *N*-succinic acid △. *N*/5-H_2SO_4 + *N*-aminoacetic acid ✱. *N*/5-H_2SO_4 + *N*/10-tyrosine ●. *N*/5-H_2SO_4 + *N*-malonic acid +. *N*/5-H_2SO_4 + *N*-formic acid ×. *N*/5-H_2SO_4 + *N*-oxalic acid ●.

malonic acid, all these acids oxidise more rapidly on the promoted Fe–C–N and Fe–C areas than on pure charcoal. The poisoning of the promoted charcoal in the case of malonic acid is attributed to the hydroxy-acid formed as an intermediate oxidation product.

The velocities of oxidation at their respective maximum rates are shown to follow the order of depolarisation for oxygen liberated at a platinum electrode.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

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