375. *Studies in Chemisorption on Charcoal. Part VIII. The Influence of Temperature of Activation of Charcoal on* (a) *Catalytic Oxidation of Salts,* (b) *Catalytic Decomposition of Hydrogen Peroxide.*

By Alexander King.

(a) *Catalytic Oxidation of Salts.*—The catalytic action of charcoal was first noticed by Calvert (J., 1867, **20**, 293), who demonstrated the oxidation of alcohol, ethylene, hydrogen sulphide, etc., by this means. Feigl (*Z. anorg. Chem.*, 1921, **119**, 305) described the oxidation of some sixteen inorganic substances on charcoal, but his results have been severely criticised by Oryng (*Kolloid-Z.*, 1925, **36**, 287) on the ground that the effects noticed were not entirely due to the presence of the catalyst.

It is now generally accepted that catalytic oxidation on charcoal is to be ascribed to the film of chemisorbed oxygen with which the substance is normally coated, and Rideal and Wright (J., 1925, **127**, 1347; 1926, 1813, 3182), by means of a poisoning method, have shown that three different types of surface oxide, differing in catalytic properties, may coexist on the carbon surface.

Several investigators (Kruyt and de Kadt, *Kolloid-Z.*, 1929, **47**, 44; *Kolloid.-Beih.*, 1931, **32**, 249; King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1094) have discussed the influence of the temperature of heating of charcoals in oxygen on their fundamental properties. Samples heated in the neighbourhood of 450° are acid in character and adsorb bases from solution, but those heated at 850° are alkaline and do not permit of any alkali adsorption; the nature of the adsorption isotherm for water differs markedly in the two types. Kolthoff (*J. Amer. Chem. Soc.*, 1932, **54**, 4473), in contrasting the properties of two charcoals prepared from the same sample but activated severally at 400° and 950°, found that the latter had a distinctly higher activity in the oxidation of ferrocyanide.

A study has now been made of the oxidation of potassium ferrocyanide, sodium arsenite, potassium nitrite, and quinol in the presence of charcoals activated in oxygen at 16 different temperatures. No attempt has been made to differentiate between the different types of oxide which may have been present at the same time on the carbon surface, as was done by Rideal and Wright, only a general relationship between catalytic activity and temperature of activation being sought. The results are in Table I, together with the adsorptive capacities of all the charcoals for iodine and their activities for the decomposition of hydrogen peroxide (see p. 1690). The results are expressed in terms of c.c. of solution oxidised by 1 g. of charcoal in 30 minutes. (The values in parentheses are discussed on p. 1689.)

It is immediately obvious from the table that the catalytic activity of charcoal is fundamentally influenced by the type of oxide surface, for in each case a maximum activity is reached with samples activated about 450°, which is the temperature recorded by several workers as optimum for the existence of the acidic surface oxide of carbon. The catalytic activity of charcoals activated above 450° decreases rapidly as the temperature of activation is increased, until at about 850° it is almost zero; above that temperature it is developed again to a slight, but definite, degree. In a previous paper (J., 1935, 889) it was reported that the p_H of charcoal suspensions in conductivity water show a maximum for samples activated in the region of 850°; it seems therefore that minimum catalytic activity corresponds to maximum alkalinity.

During the course of this work it was invariably found that the catalytic effect of a given sample of charcoal is directly proportional to the weight used. Now, activation

TABLE I.

Activation no.	1	2	3	4	5	6	7	8	9	10
Temp.	240°	320°	350°	360°	420°	490°	540°	590°	660°	690°
I_2 adsorption, c.c. *N*/10	23·6	24·0	35·0	28·8	35·0	40·2	46·4	47·0	43·0	43·6
$K_4Fe(CN)_6$ oxidised,	0·3	3·8	7·7	6·9	17·4	13·6	7·4	4·7	2·0	2·4
c.c. *N*/100	(0·013)	(0·158)	(0·22)	(0·24)	(0·53)	(0·34)	(0·16)	(0·10)	(0·047)	(0·054)
Na_3AsO_3 oxidised, c.c.	1·4	1·9	4·8	4·1	5·3	4·9	5·0	—	4·0	2·8
N/10	(0·059)	(0·079)	(0·137)	(0·141)	(0·152)	(0·122)	(0·108)	—	(0·93)	(0·064)
KNO_2 oxidised, c.c.	0·3	1·1	3·7	3·3	4·6	2·7	1·7	—	0·8	0·6
N/10	(0·013)	(0·046)	(0·105)	(0·114)	(0·132)	(0·067)	(0·036)	—	(0·019)	(0·014)
$C_6H_6O_2$ oxidised, c.c.	1·0	4·2	6·8	6·1	10·5	8·3	5·9	3·5	3·2	2·0
N/100	(0·04)	(0·17)	(0·19)	(0·21)	(0·30)	(0·23)	(0·13)	(0·075)	(0·07)	(0·046)
H_2O_2 decompn., c.c.	21·5	15·1	6·4	5·2	5·7	7·6	15·3	41·0	39·7	46·2
O_2 evolved	(0·92)	(0·63)	(0·18)	(0·18)	(0·16)	(0·19)	(0·33)	(0·87)	(0·92)	(1·06)

Activation no.	11	12	13	14	15	16	17	18
Temp.	740°	780°	830°	900°	920°	1130°	920°/500°	420°/850°
I_2 adsorption, c.c. *N*/10	48·1	25·6	54·0	49·2	21·8	37·6	31·6	41·3
$K_4Fe(CN)_6$ oxidised, c.c.	2·0	0·6	0·6	1·2	2·0	3·8	10·2	0·9
N/100	(0·041)	(0·023)	(0·011)	(0·024)	(0·091)	(0·11)	(0·32)	(0·022)
Na_3AsO_3 oxidised, c.c.	1·8	0·6	0·4	0·5	0·6	3·0	3·7	0·7
N/10	(0·041)	(0·024)	(0·007)	(0·011)	(0·027)	(0·08)	(0·117)	(0·017)
KNO_2 oxidised, c.c. *N*/10	0·0	0·0	0·0	0·2	0·2	1·4	1·6	0·0
	(0·00)	(0·00)	(0·00)	(0·004)	(0·009)	(0·037)	(0·05)	(0·00)
$C_6H_6O_2$ oxidised, c.c.	1·9	0·9	0·8	1·0	0·7	2·5	6·2	1·3
N/100	(0·039)	(0·035)	(0·015)	(0·02)	(0·03)	(0·07)	(0·20)	(0·03)
H_2O_2 decompn., c.c. O_2	56·1	32·9	77·3	51·2	46·7	60·2	(see Fig. 1)	
evolved	(1·16)	(1·29)	(1·43)	(1·12)	(2·14)	(1·62)		

at different temperatures and with different times and rates of flow of oxygen will produce charcoals of different surface area available for adsorption and catalysis. These factors have been widely varied in the present work in order to accentuate surface area differences, but care has always been taken that the treatment should be sufficiently prolonged in order to establish the type of surface characteristic of the temperature. For instance, activation no. 3 at 350° gave an iodine adsorption of 35·0 c.c.; no. 13 at 830°, 54·0 c.c.; and no. 12, activated at 780° in a very slow oxygen stream, only 25·6 c.c. In order to obtain a true comparison, therefore, the catalytic activities should be expressed in terms, not of unit weight, but of unit area of charcoal. The surface area is most conveniently found by measuring the amount of adsorption on it, but as the temperature of activation has been varied so much, an adsorbate had to be chosen which would be adsorbed to an equal extent on both acid and alkaline charcoals and therefore give an adsorption value proportional to the extent of surface and not influenced by its constitution. Acids, alkalis, and most salts must thus be excluded, but iodine has been found to give consistently satisfactory results. In view of this, the iodine values recorded in Table I can be taken as proportional to the surface areas of the charcoals concerned.

The catalytic activities *per unit area* are expressed comparatively by the numbers in parentheses in Table I, where the volumes of reagent oxidised per g. of charcoal are divided by the amount of iodine adsorbed per g. The results are even more striking than before, the high activity with acid charcoals and low activity with alkaline charcoals being very marked. Especially interesting are the results of activations 17 and 18, in which a high-temperature charcoal was reactivated at 500° and an acid (420°) charcoal reactivated at 850°. In the former case, reactivation caused an increase in the catalytic activity, and, in the latter case, a decrease, which was very marked especially in contrast with the iodine adsorption which, as might be expected, increased on reactivation. Hence, a charcoal which had a relatively high initial activity for the oxidation of potassium nitrite became incapable, after reactivation, of effecting any oxidation whatsoever in spite of a considerable increase in surface area. The catalytic activity of charcoal in oxidation reactions, like so many of its other properties, is thus undoubtedly a function of the temperature of activation.

In his work on the oxidation of ferrocyanide, Kolthoff (*loc. cit.*) found that high-temperature activation resulted in a catalytically active product, which is exactly the reverse of what has now been found. His oxidations were carried out in buffer solutions (it having been shown that the rate of oxidation increases with increasing p_H), which counteracted the alkaline nature of the high-temperature-activated charcoal; no notice was taken of the relative surface areas of the charcoals employed. In the present work the pure reagents were merely dissolved in distilled water, the acidity or alkalinity of the surface being regarded as an essential property under investigation and hence not to be neutralised by the use of buffers.

(b) *Catalytic Decomposition of Hydrogen Peroxide.*—Filippi (*Arch. Farm. sperim.*, 1907, **6**, 363) noted that the decomposition of hydrogen peroxide was accelerated by the presence of any powdered substance, and Lemoine (*Compt. rend.*, 1916, **162**, 729) examined the effect, using different sorts of charcoal as catalyst. Firth and Watson (J., 1923, **123**, 1750; *J. Physical Chem.*, 1925, **29**, 987), having examined the decomposition on charcoals prepared and activated in numerous different ways, concluded that, for both pure and impure charcoals, high sorptive capacity is not necessarily accompanied by high catalytic activity towards hydrogen peroxide. A similar view was expressed by Skumburdis (*Kolloid-Z.*, 1931, **55**, 156).

That the sorptive capacity really is proportional to the catalytic activity for activation at a given temperature is shown by the results (Table II) for a charcoal prepared at 750° and activated at 800°. The ratio of the oxygen evolution to the iodine adsorption is roughly constant throughout. Similar results have been obtained at other temperatures. On a given type of charcoal surface, therefore, the catalytic activity is proportional to the area of the surface, the apparently anomalous results obtained with charcoals of different types being due to the different types of surface which they possess in virtue of the different methods, and in particular, different temperatures, of activation. That this conclusion has some justification is shown by results of Fowler and Walton (*Rec. trav. chim.*, 1935, **54**, 476), who found that a high-temperature-activated charcoal lost the greater part of its activity for the decomposition of hydrogen peroxide on being reheated at 400°; this, it is suggested, may be interpreted on the same basis as Kolthoff's results. It is noteworthy that with impure charcoals more complicated results are to be expected, preliminary experiments having shown that the promoter action of iron and nitrogen impurities, introduced into pure charcoal, may lead to variations in the catalytic activity greater than those due to different methods of activation.

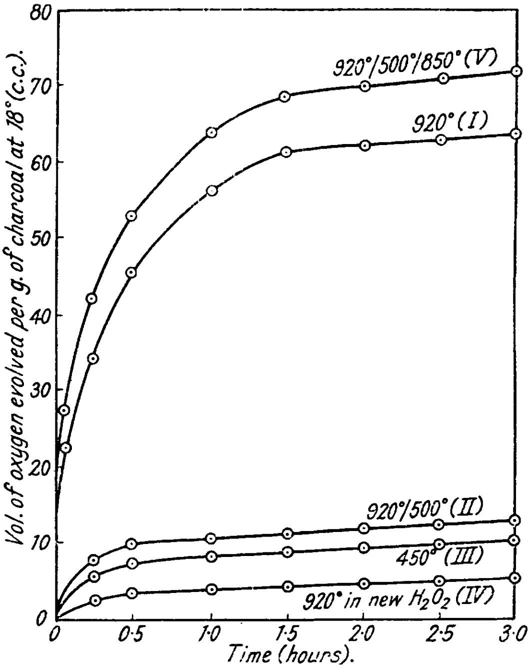
TABLE II.

Time of activation, hrs.	0	2	4	6	8	10	12	14	24
C.c. $N/10$-I_2 adsorbed per g. charcoal	19·4	35·6	43·3	48·7	51·5	52·9	53·2	53·4	50·8
C.c. O_2 evolved per g. charcoal in 30 mins.	26·2	45·2	60·2	65·7	70·5	73·0	74·5	74·2	72·1
Ratio	1·35	1·27	1·38	1·35	1·37	1·38	1·40	1·39	1·42

In the hope of explaining why pure charcoals active for sorption are not necessarily catalytically active, the rate of decomposition of hydrogen peroxide has now been measured with the series of charcoals activated at different temperatures. The values given in Table I represent the volume of oxygen evolved in ½ hour by a given quantity of hydrogen peroxide in contact with 1 g. of charcoal, the values in parentheses being the ratio to the iodine adsorption. Again, the 450° region of activation is prominent, this time as giving rise to charcoals of minimum activity. The activity steadily increases at temperatures above this value, falling again for very high temperatures. This decrease in activity can scarcely be ascribed to graphitisation, for the oxidation of the inorganic salts was accelerated in this region and the iodine adsorption values did not fall off noticeably. Some results are shown in more detail in the figure. The 920° activation curve shows that the activity of the charcoal, which is very high at first, rapidly becomes lower, there being only a slow evolution of oxygen after 2 hours. This is in agreement with the work of Firth and Watson (*loc. cit.*), who denote the initial gas evolution as α-activity, and the slow, final evolution as β-activity. The amount of oxygen evolved after 3 hours often represents only a small fraction of the total volume evolved, and this total is only a fraction of that available from the peroxide. Curve IV shows that the mere transference of a sample of charcoal, which has lost its α-activity, to a new quantity of peroxide does not result in any restoration of its α-activity.

It has been suggested (Skumburdis, *loc. cit.*) that the high, initial rate of decomposition is due to the heat of wetting of the charcoal in the peroxide solution, for the reaction is known to have a fairly high temperature coefficient. A few measurements were made of the heat of wetting in the solution employed, and it was found that the resulting rise of temperature was so small as to be entirely negligible. More probable is the hypothesis that the decrease in activity results from a preferential (physical) adsorption of oxygen on the charcoal, and hence a decrease in the area available for the adsorption of peroxide. The 450° charcoal (curve III), however, although possessing a relatively high surface area initially available for the adsorption of hydrogen peroxide, has but little α-activity. It seems more likely, therefore, that the source of the α-activity (and the reason for its disappearance) should be sought in the difference between the 450° and the 920° charcoal, *viz.*, in the manner in which the oxygen is chemically bound to the two surfaces or in the resulting acidity or alkalinity. This view is supported by the fact that a suspension of a definitely alkaline, 920°-activated charcoal gave, after treatment with hydrogen peroxide followed by thorough washing with conductivity water, a p_{H} of 4·5: treatment of the alkaline charcoal with hydrogen peroxide had converted it into the acid 450° condition with consequent loss of α-activity. It should be noticed from the figure that the β-activities of all the samples of charcoal examined were approximately the same, being presumably that of normal inactive powders.

The effect of reactivation on the catalytic activity of the charcoals is well illustrated in the figure, the activity of a 920° sample (curve I) decreasing to a large extent on reactivation at 500° (curve II) in spite of the increase in surface area; on a second reactivation at 850° (curve V), the initial activity of the sample was exceeded.



The adsorption of non-electrolytes on a surface is maximum at the isoelectric point. Hydrogen peroxide, being almost entirely undissociated in aqueous solution, should therefore follow this rule and give a maximum decomposition at this point. Rideal and Wright (*Trans. Faraday Soc.*, 1928, **24**, 530) found this to hold for a number of surfaces, including charcoal. Hence it would seem that, in the series studied above, that charcoal whose surface conditions in the presence of hydrogen peroxide solution lead to the establishment of conditions most nearly isoelectric should give a maximum adsorption and decomposition of the peroxide. This would correspond to the maximum found with high-temperature activations. It may be more satisfactory to regard the α-activity of charcoal in the decomposition of hydrogen peroxide, not as a catalysis, but merely as a reaction between the high-temperature, alkaline surface oxide of carbon and the peroxide, with the formation of the acidic surface oxide and molecular oxygen.

EXPERIMENTAL.

Pure sugar charcoal was prepared by the combustion of A.R. sucrose in a silica basin, followed by grinding, and evacuation of the product at 750° in a silica tube. The charcoal was then ground in an agate mortar and screened to **100—200** mesh. As the ash content of the product was only 0·02%, it was considered unnecessary to subject it to any treatment with acid. The charcoal was activated by heating in a silica tube furnace in the presence of moist oxygen in the manner previously described (King and Lawson, *Kolloid-Z.*, **1934**, **69**, 27).

Samples of charcoal of approximately 1 g. were weighed into steamed-out Pyrex bottles, 50 c.c. of the reagent to be oxidised were added from a pipette, and oxygen bubbled through at a standard rate of 3 bubbles per second for ½ hour. As this was sufficient to stir the liquid efficiently and to keep the solid in suspension, no mechanical agitation was employed. In each individual experiment a bottle with 50 c.c. of the reagent but containing no catalyst was attached in series with the other, so that it received the same volume of oxygen; the amount of substance oxidised in the blank experiment is in every case deducted from the amount oxidised in the presence of charcoal. This precaution was neglected by some of the previous workers (*e.g.*, Feigl, *loc. cit.*).

The partly oxidised solutions were now filtered from charcoal, the first runnings being neglected, and 25 c.c. samples analysed in the appropriate volumetric manner. For quinol, Valeur's method (*Compt. rend.*, 1899, **129**, 552) was used.

The hydrogen peroxide employed was Merck's " Perhydrol," distilled and stored in steamed-out Pyrex vessels; it was diluted five times immediately before use. The apparatus used for the decomposition of the peroxide consisted of a bottle containing a three-holed stopper which carried a tube leading to the gas burette, a stirrer operating through a mercury seal, and a wide tube for the introduction of charcoal. 25 C.c. of peroxide solution were poured into the bottle, and allowed to come to equilibrium in a thermostat at 18°, the charcoal being suspended in a small glass tube at the same temperature. The charcoal was then quickly poured into the reaction vessel through the wide tube, which was then closed by a small bung. The time required for this operation was about 3 seconds, any error due to gas evolution during this time being negligible. The solution was stirred at a constant rate throughout, it having been found, in agreement with Fowler and Walton, that the rate of gas evolution was dependent on the amount of agitation. In each case a blank experiment was run, and the volume of oxygen evolved subtracted from that of the catalysed reaction.

A series of experiments was carried out to verify that the volume of oxygen evolved was proportional to the weight of charcoal used. The results for a 780°-activated charcoal were as follows:

Wt. of C, g.	0·217	0·438	0·723	1·006	1·561	2·34
Vol. of O_2, c.c.	7·1	15·0	23·9	33·1	50·6	77·6
Vol. per g. of C.	32·7	32·9	33·2	32·9	32·4	33·1

In view of these results, the volumes of oxygen evolved are in each case calculated on the basis of 1 g. of charcoal: they are also reduced to *N.T.P.*

SUMMARY.

The catalytic oxidation of potassium ferrocyanide, sodium arsenite, potassium nitrite, and quinol was carried out, charcoals activated at 16 different temperatures being used. A maximum activity was found with charcoals activated in the region of 450°, and a minimum about 850°.

The catalytic decomposition of hydrogen peroxide by the same charcoals was studied, it being found that a minimum occurs in the 450° region and a maximum about 900°.

The results are interpreted on the basis of the existence of at least two surface oxides of carbon.

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