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PROPERTIES OF ACTIVE CHARCOAL REACTIVATED IN OXYGEN AT 400°

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Charcoal activated at high temperatures does not adsorb alkali hydroxide from aqueous solutions. This fact first stated by F. E. Bartell and E. J. Miller¹ has been confirmed later by various investigators. H. R. Kruyt and G. S. de Kadt² noticed that active charcoal heated for some time in the presence of oxygen at 400° acquired acid properties and adsorbed sodium hydroxide. Since the adsorbent and catalytic properties of charcoal seem to depend very much upon its method of preparation and since little is known of the form in which oxygen is present at the surface of the carbon, a more detailed study was made of the properties of active charcoal, the surface of which showed an acid character.

Experimental

Three kinds of charcoal were used in this work. Active sugar charcoal was prepared from ash-free sugar in a way similar to that of Bartell and Miller.¹ Another product was "Carbo medicinalis Neu Merck" made ash free according to the directions of Miller,³ the adsorbent properties of which have been described in a previous paper.⁴ A third product was Nuchar, obtained from the Eastman Kodak Company. After extraction with hydrochloric acid and hydrofluoric acid and reactivation at 950°, the ash content was 0.1%. None of these products adsorbed sodium hydroxide from 0.01 *N* solution after activation at 900 to 950°, whereas all three adsorbed inorganic acids from their aqueous solutions.

Formation of "Acid Substance" on the Surface of Charcoal by Heating in Oxygen.—Samples of the various kinds of charcoal activated at 950°

¹ Bartell and Miller, *THIS JOURNAL*, **44**, 1866 (1922); **45**, 1107 (1923); *J. Phys. Chem.*, **28**, 992 (1924); Miller, *THIS JOURNAL*, **46**, 1150 (1924); **47**, 1270 (1925); Bull. No. 73, Agricultural Experiment Station, Michigan State College, 1925.

² Kruyt and de Kadt, *Kolloid Z.*, **47**, 44 (1929); *Kolloid Beih.*, **32**, 249 (1931); G. S. de Kadt, Thesis, Utrecht, 1929.

³ E. J. Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

⁴ I. M. Kolthoff and E. van der Goot, *Rec. trav. chim.*, **48**, 265 (1929).

were heated at various temperatures in an alundum boat in an electrically heated Pyrex or quartz tube in a slow stream of dry and moist oxygen, respectively. After the indicated time of heating, the loss in weight and the adsorbent properties toward 0.01 *N* sodium hydroxide were determined. The reproducibility of the experiments depends upon the amount of charcoal heated; the formation of the acid substance is to be attributed to a surface reaction. If two boats were placed one after the other, the charcoal in the first invariably contained much more of the acid substance than the sample in the second.

It may be mentioned that at temperatures between 100 and 200° the combustion of the charcoal took place very slowly. After a prolonged time of heating at 200°, the charcoal increased in weight slightly (0.5 to 2%) in spite of the slight losses by combustion. This indicates that part of the oxygen is fixed on the surface; it is not removed after prolonged heating in a vacuum at 200°. This fixed oxygen has no acid properties. No change in the properties of charcoal was noticed if samples outgassed at 900–1000° were heated in oxygen-free nitrogen between 100 and 600°.

Experiments with Sugar Charcoal: 1-1.5-g. Samples.—In the adsorption experiment 0.5 g. was shaken with 50 cc. of 0.01 *N* sodium hydroxide and the alkalinity determined in 25 cc. of filtrate. The results are given in Table I.

TABLE I
SUGAR CHARCOAL HEATED IN DRY OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of C in %	Milliequiv. NaOH ads. by 1 g. of carbon
200	6	−0.2	0.03
250	6	−.3	.04
300	6	.2	.16
350	6	2.5	.4
400	6	2.5	.7

In Table II some results are given of experiments with Merck charcoal. With Eastman's charcoal practically the same results were obtained.

From the results it may be inferred that the best way of preparing charcoal, whose surface is practically saturated with the acid substance, is by heating small samples of the activated products (about 1 g.) for six hours in a slow current of dry oxygen at about 400°.

It seems that the initial formation of this acid takes place slowly, but when once started it progresses rapidly. Water vapor seems to promote the oxidation and the formation of the acid substance. In the following experiments Merck charcoal (freshly heated for six hours to 950°) was treated with purified oxygen, which had been saturated with water vapor at 25° by passing through three wash bottles containing water.

Acid is also formed at lower temperatures in the presence of water. Half-gram samples of Merck charcoal (freshly heated to 950°) were heated

TABLE II
MERCK CHARCOAL HEATED IN DRY OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of carbon in %	Grams of carbon shaken with 50 cc. of 0.01 <i>N</i> NaOH	Milliequiv. NaOH ads. by 1 g. of carbon
200	6.5	-2	0.5	0.032
250	6	-2	.5	.06
300	6	3	.5	.20
300	6.5	0.5	.5	.08
350	3	4	.5	.47
350	6	20	.25	1.04
380	6	28	.25	1.00
400	6	20	.25	0.96
450	3	2	.25	.10
450	6	50	.25	1.36
450	6	45	.25	1.12
500	3	2	.5	0.2
500	6	90		
550	3	98		

TABLE III
MERCK CHARCOAL HEATED IN MOIST OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of carbon in %	Grams of carbon shaken with 50 cc. of 0.01 <i>N</i> NaOH	Milliequiv. NaOH ads. by 1 g. of carbon
200	6	32	0.5	0.54
250	6	37	.5	.64
300	6	60	.5	.84
350	6	85	.1	3.6

in a Pyrex flask with conductivity water, purified air being passed through the boiling suspension.

After two days the charcoal was collected, filtered and shaken with 0.01 *N* sodium hydroxide; 0.088 milliequivalent of the latter was adsorbed by 1 g. of charcoal. If the suspension was boiled for a week this figure increased to 0.2 milliequivalent. Formation of acid even took place at room temperature if the charcoal was left in not too dry an atmosphere.

Samples of Merck charcoal (freshly heated to 950°) were kept in desiccators over water, deliquescent sodium bromide and concentrated sulfuric acid, respectively, for six months. The sample kept over sulfuric acid did not adsorb any sodium hydroxide, that kept over sodium bromide 0.08 milliequivalent per 1 g. of carbon, and the one kept over water 0.075 milliequivalent.

In agreement with the statement of Kruyt and de Kadt² it was noticed that charcoal heated in oxygen at 400° is wetted much more easily by water than after activation at 900°. It seems that the acid formed changes the hydrophobic character of the charcoal into a hydrophilic one.

The difference in hygroscopic character between charcoal activated at 950° and samples reheated for six hours in dry oxygen at 400° is shown by

the following experiments.⁵ Freshly heated samples were placed in desiccators of various humidities at room temperature. The increases in weight are given in Table IV.

TABLE IV
HYGROSCOPIC CHARACTER OF C950 AND C400

Relative water vapor tension	Time of standing in days	Water content in % C950	Water content in % C400
100 (water)	18	38.4	53
100	28	40.0	53
60	18	12.5	29.2
60	28	12.4	30.5
0 (H ₂ SO ₄)	18	0.0	0.0
0	28	0.0	0.0

Stability of the Acid on the Surface.—Weighed samples of C400 were heated at various temperatures in a high vacuum, cooled, saturated with dry air and weighed in a closed weighing bottle. 0.25-g. samples were shaken with 50 cc. of 0.01 *N* sodium hydroxide in order to determine whether the acid content of the C400 had decreased during the heating. It appeared that the acid on the charcoal was quite stable in a vacuum at temperatures below 500°. Even after heating for thirty hours at this temperature the adsorbed amount of base was the same as that adsorbed by the original C400. After heating for twenty-four hours at 575° a slight decrease in weight was noticed and the adsorption of sodium hydroxide showed a marked decrease. The original sample adsorbed 1.04 milliequivalents of base per 1 g., whereas after twenty-four hours of heating at 575° this amount decreased to 0.4 milliequivalent. After heating for twenty-four hours at 600°, 0.03 to 0.12 milliequivalent was adsorbed by 1 g. of charcoal.

From these experiments it may be inferred that the acid or acid oxide present on the C400 decomposes slowly at temperatures between 575 and 600°. At higher temperatures this decomposition takes place much more rapidly.

Properties of the "Acid Charcoal."—In many respects the properties of the charcoal the surface of which has an acid nature (C400) are quite different from those of carbon activated at 900 to 1000° (C950). C400 adsorbs strong bases; C950 does not, and may even give a negative adsorption. A suspension of C400 in water is negatively, a similar suspension of C950 is positively, charged.^{3,6}

Hydrolytic Adsorption by C400.—If C950 is shaken with an inorganic salt solution a hydrolytic adsorption of the acid takes place and the filtrate

⁵ In the following work ash-free Nuchar was used. Samples freshly heated for six hours at 950° will be designated as C950; those treated afterward for six hours in oxygen at 400° as C400.

⁶ S. Roychoudhury, *J. Ind. Chem. Soc.*, **8**, 433 (1931).

has an alkaline reaction (Bartell and Miller¹). If C400 is shaken with an inorganic salt solution, the filtrate has an acid reaction. 1.5 g. of C400 was shaken with 50 cc. of 0.01 *N* sodium chloride.

The filtrate had a *PH* of 3.5, 25 cc. taking about 8.2 cc. of 0.01 *N* barium hydroxide with phenolphthalein as an indicator. The color change was very vague, although the filtrate had been freed from carbon dioxide; near the end-point the appearance of a slight brownish turbidity was noticed. The small hydrogen-ion concentration and the high titration acidity together with the vague color change of the indicator show the presence of a very weak acid in the filtrate. The acid reaction found in the filtrate therefore cannot be attributed to a hydrolytic adsorption of the base by C400, liberating an equivalent amount of hydrochloric acid. By a chloride titration of the filtrate it was shown that only a slight trace of the anion was adsorbed by the charcoal (0.02 milliequivalent Cl by 1 g.). The experiments show conclusively that part of the acid substance present on the surface of C400 is removed by shaking with a salt solution. It is of interest to note that even the extract of C400 in pure water had an acid reaction: 1 g. of C400 was shaken with 50 cc. of conductivity water, the filtrate had a *PH* of 4.3 (the original water of 5.8); 25 cc. took 1 cc. of 0.01 *N* sodium hydroxide with phenolphthalein as an indicator (vague color change). From these and other experiments it is inferred that there is a definite chemical compound with acid properties present at the surface of C400. Attempts to identify the nature of this acid have failed so far; larger quantities of material are required for this purpose.

Adsorbent Properties of C400 as Compared with those of C950 toward Acids.—The results of a few adsorption experiments are given in Table V. A more detailed report of the adsorption of organic acids by C400 and C950 with regard to the applicability of Traube's rule will be given in a later communication.

TABLE V
ADSORPTION OF ACIDS BY C400 AND C950

Amount of charcoal used, g.	Solution used in adsorption experiment	Milliequivalents of acid adsorbed by 1 g.	
		C400	C950
0.25	50 cc. 0.01 <i>N</i> hydrochloric acid	0.00	0.41
.5	50 cc. 0.01 <i>N</i> hydrochloric acid	— .01	.36
.25	50 cc. 0.01 <i>N</i> sulfuric acid	— .08	.57
.25	50 cc. 0.01 <i>N</i> molar phosphoric acid	— .02	.30 (m. mols.)
.25	50 cc. 0.01 <i>N</i> acetic acid	— .04	.81

The apparent slight negative adsorption of the acids by C400 has to be attributed to the extraction of some of the acid from the surface of the charcoal. By a chloride determination in the filtrate it was shown that no hydrochloric acid was adsorbed by C400. By heating the latter product for twenty-four hours in a vacuum at 620°, it assumed the properties of

C950. The acid had been removed from the surface and it adsorbed inorganic and organic acids almost to the same extent as C950.

The adsorbent properties of C400 and C950 toward iodine were also determined. The adsorption by the former was distinctly less than that by the latter, but the difference was of a quite different order than that of the acids.

Peroxide in C950 and C400.—A. B. Lamb and L. W. Elder, Jr.,⁷ found that the extract obtained by shaking dilute sulfuric acid with activated coconut charcoal contained a trace of peroxide. The filtrate obtained by us after shaking C950 and C400 with *N* sulfuric acid also contained a trace of peroxide, as shown by the potassium iodide–starch test; the reaction in the filtrate of C400 being distinctly less intense than that in the filtrate of C950. The same results were obtained in the filtrates obtained by successive extractions, but the difference in behavior between both types of charcoal was very small.

Catalytic Effect of Charcoal on Oxidation by Oxygen.—It is well known that charcoal promotes oxidation. A. Kutzelnigg⁸ showed that "carbo medicinalis Merck" (ash 2.53%) favors the air oxidation of potassium ferrocyanide. The experiments with this reagent can be conducted in a simple way; it appeared, however, that the results are very much dependent upon the *P_H* of the solution. In preliminary experiments 0.25 g. of C400 and of C950, respectively, were shaken for fifteen minutes with 50 cc. of a freshly prepared 0.05 molar ferrocyanide solution in conductivity water. In 25 cc. of filtrate the ferrocyanide content was determined iodimetrically. The blank after the same time of shaking required 1.75 cc. 0.01 *N* thiosulfate, the filtrate of C950 0.83 cc., that of C400 4.03 cc. of 0.01 *N* reagent. The conclusion that C400 promotes the air oxidation of ferrocyanide more than C950 is not warranted, as is shown below. The difference in the behavior between the two kinds of charcoal is explained by the fact that a hydrolytic adsorption takes place on shaking the ferrocyanide with C950, whereby the solution becomes alkaline, whereas the C400 gives the solution a distinct acid reaction. In order to get a comparable result, 0.25 g. of charcoal with 50 cc. of the solution was first shaken for thirty minutes, then transferred into glass cells through which purified oxygen gas was bubbled with a velocity sufficient to keep the charcoal in suspension for one hour. In order to have the same conditions, the suspension of C400, that of C950 and the blank were placed in series one after the other. The results are given in Table VI.

The speed of oxidation of ferrocyanide by oxygen increases with decreasing *P_H*; charcoal activated at 900–1000° promotes this oxidation, whereas C400 hardly has any effect. The acid adsorbed on the surface of

⁷ Lamb and Elder, Jr., *THIS JOURNAL*, 53, 157 (1931).

⁸ A. Kutzelnigg, *Ber.*, 63B, 1753 (1930).

the latter therefore either spoils its oxygen electrode function or decreases the adsorption of free oxygen.

If the C400 was heated for ten hours at 620° in vacuum it acquired the same promoting effect as C950. The properties of the latter did not change on heating for ten hours at 600° in a vacuum.

TABLE VI

PROMOTING ACTION OF C950 AND C400 ON OXIDATION OF FERROCYANIDE BY OXYGEN

Composition of solution containing 0.025 molar ferrocyanide	P _H of mixture	Cc. of 0.01 <i>N</i> thiosulfate by 25 cc. of filtrate		
		C400	C950	Blank
0.05 <i>N</i> HCl	Appr. 1.5	16.90	67.90	10.32
0.1 <i>N</i> acetic acid	Appr. 3.0	15.23	63.91	16.31
Phthalate buffer	3.0	12.50	55.60	13.03
Phthalate buffer	4.0	10.00	46.72	9.95
Phthalate buffer	5.0		23.40	5.27
Phthalate buffer	5.0	6.00	26.97	6.25
Phthalate buffer	6.0	...	30.65	4.40
Phosphate buffer	6.0	...	26.97	6.25
Phosphate buffer	6.0	...	27.91	3.00
Phosphate buffer	7.0	...	16.20	1.45
Phosphate buffer	8.0	...	5.53	1.37

Decomposition of Sodium Thiosulfate in the Presence of C400 and C950.—It has been noticed by I. M. Kolthoff⁹ that charcoal activated at high temperatures (900°) promotes the decomposition of thiosulfate in its aqueous solutions. A 0.01 *N* sodium thiosulfate solution in a buffer with a P_H of 6 is stable for a long time; if shaken for twenty-four hours with active charcoal (C900) no thiosulfate is present in the filtrate as indicated by the titration with iodine. Thiosulfuric acid is removed from the solution by hydrolytic adsorption, the acid decomposes at the surface of the charcoal and another fraction of the thiosulfate will be hydrolytically adsorbed. It was of interest to compare the influence of C950 and C400 on the decomposition of thiosulfate.

The surface of C400 is covered with an acid and for this reason it may accelerate the decomposition of thiosulfate; on the other hand, this charcoal no longer shows any hydrolytic adsorption of the acid of the salt; 0.25 g. of charcoal was shaken with 50 cc. of 0.01 *N* sodium thiosulfate in

TABLE VII

INFLUENCE OF C400 AND C950 UPON DECOMPOSITION OF SODIUM THIOSULFATE

Composition of 0.01 <i>N</i> Na ₂ S ₂ O ₃ solution	Time of shaking in hours	Cc. of 0.01 <i>N</i> iodine required by 25 cc. of filtrate	
		C400	C950
Water	3	20.00	21.20
Water	24	13.00	6.75
Phosphate buffer P _H 6.0	3	14.10	2.40
Phosphate buffer P _H 6.0	24	0.25	0.00

⁹ I. M. Kolthoff, *Rec. trav. chim.*, **48**, 298 (1929).

water or in a phosphate buffer with a P_H of 6.0. The blanks without charcoal did not change their strengths during the course of the experiments. A few results are given in Table VII.

In spite of the presence of the acid substance at the surface of the C400 the latter has less promoting effect upon the decomposition of thiosulfate than C900 has.

Summary

Charcoal activated at 900 to 1000° and heated thereafter in oxygen at 300 to 500° forms at its surface a definite chemical compound with acid character. The optimum temperature for preparing this "acid charcoal" is 400°. The acid on the surface is stable in a vacuum at temperatures as high as 500–550°. The "acid charcoal" is much more hygroscopic than the product activated at 950°.

The adsorbent and catalytic properties of the "acid charcoal" are quite different from those of carbon activated at 900–1000°

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE
UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN UNI-UNIVALENT CHLORIDE SOLUTIONS AT CONSTANT TOTAL MOLALITY

By J. ERSKINE HAWKINS

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In this investigation the electromotive force of cells of the following types was measured

(A) $H_2/HCl(m_1)/AgCl/Ag$ and

(B) $H_2/HCl(m_1), MCl(m_2)/AgCl/Ag$

M represents either lithium, sodium or potassium and the total molality $m_1 + m_2 = 4.0, 5.0$ and 6.0 .

Harned¹ has measured cells of the same type, using calomel electrodes instead of the silver-silver chloride electrodes and where $m_1 + m_2 = 0.1, 1.0$ and 3.0 . All calculations at these concentrations are based on his measurements. Recalculations were carried out, due to a slight error which Harned² pointed out.

A few investigators³ have measured cells of the type (A) containing pure hydrochloric acid at a concentration above three molal. However, no previous determinations have been made with cells of type (B), wherein $m_1 + m_2$ is greater than three molal.

¹ Harned, THIS JOURNAL, **48**, 326 (1926).

² Harned, *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927).

³ Ellis, THIS JOURNAL, **38**, 737 (1916); Linhart, *ibid.*, **39**, 2601 (1917); Randall and Young, *ibid.*, **50**, 989 (1928).