

in 2 to produce II, or with X^- to form III, as in 3. III could subsequently react with the base to form the quaternary ion, (II), as shown in 4. In the case of the perchlorate salt, the reaction should certainly proceed by 2.

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Experimental

Diazoacetophenone.—To an ether solution of diazomethane³ was added, under cooling, a $1/3$ molar portion of benzoyl chloride with efficient stirring. After the addition was complete the solution was stirred for an additional fifteen minutes and allowed to come to room temperature. The solvent and excess diazomethane were then distilled off carefully on the steam-bath, and the solution was cooled to effect crystallization. The material was recrystallized from petroleum ether until free of halogen, m. p. 49–50°.⁴

Heterocyclic Amine Salts.—2-Picoline hydriodide was prepared according to the directions of Murrill.⁵ Quinoline hydriodide was prepared by the procedure of Trowbridge.⁶ The sulfate, phosphate, perchlorate, tosylate and the hydrohalides of pyridine and the hydriodides of

(3) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 50.

(4) Wolff, *Ann.*, **325**, 142 (1902).

(5) Murrill, *This Journal*, **21**, 831 (1899).

(6) Trowbridge, *ibid.*, **21**, 67 (1899).

isoquinoline and 3-methyisoquinoline were prepared by adding a slight excess of the appropriate acid to the base and heating on the steam-bath overnight. The cooled suspension was filtered and the product washed with a small amount of absolute alcohol. The salts were used without further purification.

Preparation of the Quaternary Salts.—The three procedures used were essentially the same for all the compounds listed in this report. The techniques employed will be illustrated by a typical example for each of the methods.

(a) To 1.46 g. (0.010 mole) diazoacetophenone in 15 cc. of ether was added 2.07 g. (0.011 mole) of pyridine hydriodide. The ether was evaporated slowly on the steam-bath and the mixture heated for one-half hour after the vigorous evolution of nitrogen had occurred. The tarry material was then treated with a small amount of water and sufficient alcohol to bring it into solution at the boiling point, decolorized with charcoal, filtered and cooled. The 1-phenacylpyridinium iodide was recrystallized from dilute aqueous alcohol.

When salts of pyridine other than the hydriodide were used in the reaction (Table II), the hot aqueous alcoholic solution of the pyridinium salt was treated with perchloric acid and the product isolated as the sparingly soluble phenacylpyridinium perchlorate. The yields reported in Table II are calculated from the amount of perchlorate salt obtained in this manner.

(b) A mixture of 1.46 g. (0.010 mole) diazoacetophenone, 2.07 g. (0.011 mole) pyridine hydriodide and 15 cc. absolute alcohol was refluxed for one hour. A small volume of water was added, the solution was decolorized with charcoal and filtered. The quaternary iodide separated on cooling, and was recrystallized as above.

(c) To 1.46 g. (0.010 mole) diazoacetophenone in 15 cc. absolute alcohol was added 2.07 g. (0.011 mole) of pyridine hydriodide and 1.5 cc. of pyridine. The mixture was refluxed for one hour. A small amount of water was added and the product was crystallized as above.

Summary

It has been demonstrated that diazoacetophenone reacts with salts of certain heterocyclic amines to produce the corresponding phenacyl quaternary salt.

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Oxygen Complexes on Charcoal^{1a}

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Introduction

It is well known that treatment of activated charcoals with oxygen produces adsorbents having properties very different from those of the untreated charcoals. Rhead and Wheeler² were apparently the first investigators to adduce extensive evidence for the fixation of oxygen on the charcoal surface. They concluded that the formation of the loosely-formed physico-chemical complex is an important step in the combustion of carbon. A similar conclusion was reached by Lambert.³

(1) (a) The work herein reported was done under a contract between the National Defense Research Committee and the University of Chicago. (b) Present address: U. S. Bureau of Mines, Bruceton, Pennsylvania.

(2) Rhead and Wheeler, *J. Chem. Soc.*, **108**, 461 (1913).

(3) Lambert, *Trans. Faraday Soc.*, **32**, 452 (1926).

Lowry and Hulett⁴ found that charcoal exposed to air at room temperature contained up to 3 to 4% oxygen; when the charcoal was outgassed at high temperatures, the oxygen was evolved as carbon monoxide and carbon dioxide.

From a study of the adsorption of acid and base adsorbed from dilute aqueous solution as a function of pressure of oxygen to which outgassed charcoal had been exposed, Schilow, Schatunowskaja and Tschmutow⁵ suggested that there are at least three distinct surface oxides; Lepin⁶ agreed with their suggestions. Two of these, they concluded, are formed by the adsorption of oxygen at room

(4) Lowry and Hulett, *This Journal*, **42**, 1408 (1920).

(5) Schilow, Schatunowskaja and Tschmutow, *Z. physik. Chem.*, **A149**, 211 (1930); **A150**, 31 (1930).

(6) Lepin, *Physik. Z. Sowjetunion*, **4**, 282 (1933).

temperature and the third at higher temperatures, notably in the neighborhood of 400–450°. The existence of two room temperature oxides was, however, denied by Burstein, Frumkin and Lawrowskaja,⁷ who showed that the hydrogen chloride adsorbed from dilute solution was stoichiometrically equivalent to the amount of oxygen actually adsorbed by the charcoal (up to an oxygen pressure of 0.1 mm.).

King and his co-workers⁸ studied charcoals activated in oxygen at temperatures from 350° to 1030°. They found that the adsorption of hydrochloric acid per unit surface increased with temperature up to about 850°, while the base adsorption decreased to zero over the same range. Above 850° base adsorption was observed to reappear to a slight extent and acid adsorption to decrease somewhat. King's results at high temperatures are open to question, however, since the samples were apparently exposed to air during cooling.

Verstraete⁹ investigated the electrokinetic properties of colloidal carbon and found that carbon assumes a positive or a negative charge in water, depending on whether it is activated at 950° or 450°, respectively. The same electrokinetic behavior was observed by Miss Bach,¹⁰ who also found that whereas charcoal activated in carbon dioxide at 950° and exposed only to air at room temperature adsorbed anions from potassium chloride solution, after treatment of the charcoal with oxygen at 350 to 450° adsorption of anions from potassium chloride diminished and adsorption of cations set in.

Bruns, Maximova and Pos¹¹ made an extensive study of the adsorption from dilute sodium hydroxide or sulfuric acid solutions by charcoals activated in carbon dioxide at 850° to varying degrees and then oxidized with air at 250, 335, 400 or 550° (measurements only of weight loss and of acid or base adsorption were made). Prior to air oxidation, acid was adsorbed from solution, but not base. As the oxidation proceeded, the base adsorption set in and continuously increased, while acid adsorption decreased ultimately to zero. Within the temperature range studied, the development of base-adsorbing power was greatest on oxidation at 400°.

The data presented in this paper constitute a further study of the materials prepared by oxidation of charcoal at 400°. Since ultimate analyses were made, it was possible quantitatively to associate variations in certain properties of the charcoals with the formation or destruction of oxygen complexes. That these complexes may be very important in understanding the behavior of oxidized charcoal is indicated by the fact that char-

coals can be produced which contain more than 18% of oxygen by weight (see below).

Experimental

Treatment with Oxygen.—Seventy-four to 136 g. of charcoal was treated in a rotating, cylindrical iron chamber equipped with internal flights. The rotation of the cylinder about its axis, at *ca.* 30 r. p. m., kept the charcoal in constant tumbling motion. Heating was accomplished by an external electric furnace. The temperature at the center of the reaction chamber was found to differ from the furnace temperature by less than 10°. The temperatures recorded below are furnace temperatures. It is probable that the temperature of individual charcoal particles rose considerably above the recorded furnace temperature for short periods during the treatment with oxygen.

Tank oxygen was used without further purification. Oxygen flow rates through the reaction chamber were measured with a capillary flowmeter.

Outgassing.—Several of the oxygen-treated samples and some untreated ones were outgassed at various temperatures for long periods. In these experiments a sample weighing about 50 g. was supported on a chromel gauze in the central portion of a long silica tube. That portion of the tube which contained the sample was surrounded by a vertical furnace. The lower end of the silica tube was closed by a solid rubber stopper, and the upper end was equipped for evacuation by a mechanical (oil-rotary) pump.

Charcoal.—A number of charcoals were studied. Since, however, the primary object was a study of the oxygen complex and not an investigation of the potentialities of the charcoal from which it was made, it seemed desirable to avoid complications due to ash content and to variations in the prior history of the carbon. For this reason most of the experiments, and all of those reported here, were performed on CWS N-19, a charcoal made from sawdust by activation with zinc chloride ($ZnCl_2$:sawdust = 0.9; primary calcination at 600°, followed by rotary calcination at 850°) which contained 0.3% ash. The individual particles of N-19 were cylinders of $1/16$ -inch diameter and approximately $1/16$ -inch length.

Determination of Acid- and Base-Adsorptive Powers.—The nature of the product formed by oxygen treatment has frequently been studied by the determination of the amounts of acids and bases adsorbed from dilute aqueous solution.^{5,7,9,10-14} As a convenient indicator of complex formation we employed the adsorption from 0.03 *N* solutions during a half-hour period of immersion. In all cases the samples were exposed to air at room temperature prior to the adsorption studies. The detailed procedures were as follows:

1. Adsorption of Base.—One gram of charcoal was shaken intermittently for one-half hour with 50 cc. of 0.03 *N* sodium hydroxide solution. Two titration procedures followed the filtration: (a) To determine the total moles of base removed by adsorption and neutralization of carbonic acid (derived from carbon dioxide on the charcoal), aliquot parts of the filtrate were titrated with hydrochloric acid in the presence of strontium chloride and phenolphthalein. (b) To determine the net base removed, *i. e.*, the total base removed minus that required to neutralize carbonic acid, aliquot parts of the filtrate were acidified with excess hydrochloric acid solution, boiled, and back-titrated with sodium hydroxide. Half the difference between (a) and (b) is equal to the moles of carbonic acid surrendered by the charcoal to the alkaline solution.

2. Adsorption of Acid.—One gram of charcoal was shaken intermittently for one-half hour with 30 cc. of 0.03 *N* hydrochloric acid solution. Aliquot parts of a filtrate from the mixture were titrated with 0.03 *N* sodium hydroxide in the presence of phenolphthalein. In a few

(7) Burstein, Frumkin and Lawrowskaja, *Z. physik. Chem.*, **A150**, 421 (1930).

(8) King, *J. Chem. Soc.*, 1489 (1937); Chambers and King, *ibid.*, 688 (1938); Bennister and King, *ibid.*, 991 (1938).

(9) Verstraete, *Natuurw. Tijdschr.*, **18**, 107 (1936).

(10) Bach, *Acta Physicochim. U. R. S. S.*, **14**, 463 (1941).

(11) Bruns, Maximova and Pos, *Kolloid Z.*, **63**, 286 (1933).

(12) Bretschneider, *Z. physik. Chem.*, **A159**, 436 (1932).

(13) Kolthoff, *THIS JOURNAL*, **54**, 4473 (1932).

(14) Kruyt and deKadt, *Kolloid-Beihfte*, **32**, 249 (1931).

control experiments the solutions were boiled before titration, but this procedure was found to be unnecessary. The carbon dioxide liberated to the acid solution by the charcoal is negligible.

As described in the discussion below, experiments were also performed on several samples in which the time of adsorption and the concentration of acid or base solution were varied. In all cases the treatment of the filtrate was identical with that given here.

Ultimate Analyses, Heats of Combustion.—Analyses for per cent. carbon, hydrogen and ash were made with the usual combustion train used in organic macroanalysis. The per cent. oxygen was obtained by difference.

Heats of combustion were determined with an adiabatic oxygen bomb calorimeter manufactured by the Parr Instrument Co. The instrument was calibrated with standard samples of benzoic acid obtained from the U. S. Bureau of Standards.

Results and Discussion

In Tables I, II and III are summarized both the conditions used in preparing some of the oxygen-treated samples and a number of their properties. CWS N-19 was the base material for all of the preparations. The final three columns of Tables I and II give the apparent adsorption from solution of hydrochloric acid and sodium hydroxide, based, however, on 0.03 *N* solutions and one-half hour periods of immersion.

Efficiency of the Oxidation Process.—For samples oxidized at 400°, the oxygen content increases continuously with increasing weight loss (*cf.* samples TUC-45, TUC-60, and TUC-46).

The oxidation process becomes less efficient, however, as the weight loss increases. The ratio of number of carbon atoms "burned away" to number of oxygen atoms added to the solid product was calculated to be 6.0, 6.1, 9.9 and 16.3 for samples TUC-45, TUC-60, TUC-34 and TUC-46, resp. The order is the same as that of increasing weight loss.

Adsorption of Acid and Base from Solution.—The progress of the oxygen treatment was conveniently followed by determination of the amount of hydrochloric acid or

sodium hydroxide which the sample could adsorb during a one-half hour immersion period in a 0.03 *N* solution of acid or base. In Fig. 1 is plotted the net amount of base adsorbed (see "Experimental"

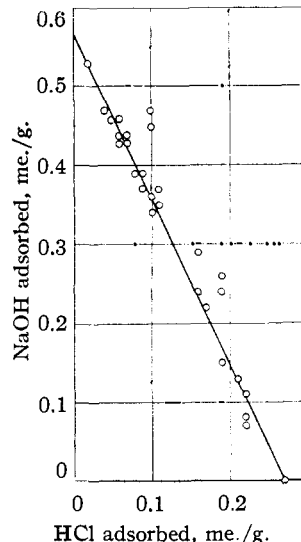


Fig. 1.—Adsorption of acid and base from solution: 0.03 *N* solutions, one-half hour contact times.

TABLE I
TREATMENT WITH OXYGEN OF CWS N-19

Product	Treatment	Hours of treatment	Per cent. weight loss	Consumption, milliequivalents per gram of		
				HCl	NaOH (total)	NaOH (net)
CWS N-19	Dried at 140°	2	..	0.27	0.00	0.00
TUC-31	360°, O ₂ , 2 l./hr.	8	4.7	.19	.30	.26
TUC-32	400°, O ₂ , 2 l./hr.	9	6.5	.16	.36	.29
TUC-33	400°, O ₂ (moist), 2 l./hr.	7.5	6.3	.19	.27	.24
TUC-40	420°, O ₂ , 2.6 l./hr.	19	17.5	.10	.47	.47
TUC-45	400°, O ₂ , 3.3 l./hr.	24	23.5	.10	.49	.45
TUC-46	400°, O ₂ , 3.7 l./hr.	32	56	.02	.59	.53
TUC-47	400°, O ₂ , 2 l./hr.	31	13	.11	.39	.37
TUC-55	400°, O ₂ , 2 l./hr.	21.5	15.3	.09	.38	.37
TUC-56	400°, O ₂ , 6 l./hr.	21	36.9	.05	.50	.46
TUC-58	400°, O ₂ , 6 l./hr.	6.6	11.4	.11	.41	.35
TUC-60	400°, O ₂ , 12 l./hr.	10	25	.08	.50	.39
TUC-61	400°, O ₂ , 12 l./hr.	11	33	.06	.56	.43
TUC-62	400°, O ₂ , 6 l./hr.	21	21	.09	.48	.39
TUC-65	400°, O ₂ , 12 l./hr.	9.2	25	.07	.53	.43
TUC-72	400°, O ₂ , 3 l./hr.	3	0.9	.22	.16	.08
TUC-78	400°, O ₂ , 1 l./hr.	15	9.4	.19	.22	.15
TUC-80	400°, O ₂ , 3 l./hr.	16.5	10	.10	.41	.34
TUC-81	400°, O ₂ , 8 l./hr.	8.5	11	.10	.47	.36
TUC-83	400°, O ₂ , 6 l./hr.	18	25	.06	.51	.44
TUC-84	400°, O ₂ , 1 l./hr.	29	4.6	.16	.31	.24
TUC-87	400°, O ₂ , 20 l./hr.	9	48.5	.06	.56	.46
TUC-95	400°, O ₂ , 1 l./hr.	17	4.2	.17	.27	.22
TUC-96	400°, O ₂ , 1 l./hr.	5	0.4	.21	.15	.13
TUC-97	400°, O ₂ , 6 l./hr.	22	32.7	.04	.54	.47
TUC-98	400°, O ₂ , 1 l./hr.	3	..	.22	.18	.07
TUC-99	400°, O ₂ , 1 l./hr.	2	0.5	.22	.11	.11
TUC-117	400°, O ₂ , 4 l./hr.	24.3	22.6	.07	..	.44

TABLE II
 HEAT TREATMENT IN VACUUM OF N-19 AND PRODUCTS OF N-19

Product	Source material	Treatment	Hours of treatment	Per cent. weight loss	Apparent density, g./cc.	Consumption, milliequivalents per gram, of		
						HCl	NaOH (total)	NaOH (net)
TUC-45	N-19	O ₂ , 400°, 3.3 l./hr.	24	23.5	0.46	0.10	0.49	0.45
TUC-48	TUC-45	Outgassed at 500°	24	5.6	.46	.14	.37	.28
TUC-49	TUC-45	Outgassed at 700°	25	8.1	..	.28	.20	.18
TUC-50	TUC-45	Outgassed at 900°	24	16.9	.47	.36	..	.04
TUC-52	N-19	Outgassed at 900°	24	1.5	.48	.29	.00	.00
TUC-53	N-19	Outgassed at 400°	24	0.8	..	.25	.00	.02
TUC-34	N-19	490°, O ₂ , 3 l./hr.	25	28.1	.41	.15	.44	.41
TUC-37	TUC-34	Outgassed, heated to 800°	1	..	.42	.29	.20	.19
TUC-36	N-19	490°, O ₂ , 3 l./hr.	24	28.2	.41	.13	.54	.49
TUC-39	TUC-36	Outgassed at 600°	18	8.4	.42	.20	.36	.35
TUC-38	N-19	490°, O ₂ , 3 l./hr.	30	30.4	.41	.12	.51	.49
TUC-41	TUC-38	Outgassed at 1050°	26	18	.45	.37	.01	.01
TUC-83	N-19	400°, O ₂ , 6 l./hr.	18	25	.45	.06	.51	.44
TUC-86	TUC-83	Outgassed at 400°	24	0.7	..	.06	.46	.42
TUC-88	TUC-83	Outgassed at 650°	24	11.4	..	.15	.32	.30
TUC-93	TUC-83	Outgassed at 900°	24	17.5	.45	.33	.05	.07

section) *vs.* the amount of acid adsorbed by the samples listed in Table I. (Net rather than total base adsorption has been used throughout, since the amount of carbon dioxide present in a sample and releasable to an alkaline solution is considered to be a somewhat accidental property of a sample.) Within experimental error the original material, CWS N-19, has no base-adsorbing power, but one gram adsorbs 0.27 milliequivalent of hydrochloric acid from a 0.03 *N* solution. Its adsorptive properties are typical of charcoals activated at high temperatures and subsequently exposed to air at room temperature.^{8,10,11,15} Treatment with oxygen at 400° increases the base adsorption and decreases the acid adsorption, in agreement with earlier findings.^{5,10,11} The most highly treated material, TUC-46, was able to adsorb only 0.02 milliequivalents of hydrochloric acid per gram (me./g.), and it appears probable that further treatment would have resulted in the limiting condition of zero acid adsorption found by Bruns, Maximova and Pos.¹¹ Figure 1 shows the close inverse relation between acid and base adsorption,

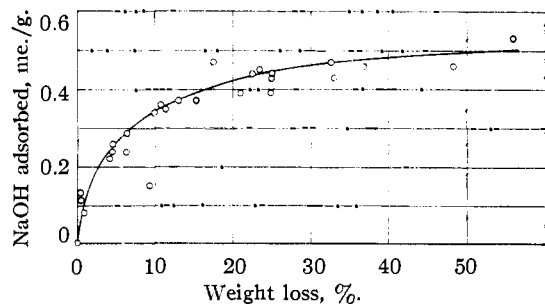


Fig. 2.—Dependence of sodium hydroxide adsorption on weight loss during oxygen treatment.

(15) Bartell and Miller, *THIS JOURNAL*, 44, 1866 (1922).

 TABLE III
 ULTIMATE ANALYSES AND HEATS OF COMBUSTION

Sample	C, %	H, %	Ash, %	O, %	$\Delta H_{comb.}$ cal./g. of sample
CWS N-19	96.0	0.65	0.3	3.1	7936
TUC-34	88.4	.61	.5	10.5	7107
TUC-37	91.8	.63	.5	7.1	7526
TUC-41	94.9	.28	1.0	3.8	7813
TUC-45	86.4	.62	0.3	12.7	6846
TUC-46	80.7	.63	.4	18.3	6333
TUC-48	87.9	.62	.4	11.1	7069
TUC-50	94.5	.65	.3	4.6	7743
TUC-52	96.3	.48	.3	2.9	7819
TUC-60	85.5	.67	.3	13.5	..
Graphite	99.7	.16	.0	.1	7829

 TABLE IV
 SURFACE AREAS OF N-19 AND PRODUCTS OF N-19

Sample	Surface area, sq. m./g. of sample
CWS N-19	1720
TUC-52	1730
TUC-45	2080
TUC-50	2020
TUC-742 (a portion of TUC-32)	1670

but the slope is not of theoretical significance because of the arbitrary adsorption conditions employed (see below).

Figure 2 shows base adsorbing power (one-half hour in 0.03 *N* solution) as a function of the extent of treatment, *i. e.*, as a function of weight loss. The power to adsorb base seems to be approaching as a limit the amount (about 0.6 me./g.) which, as shown on Fig. 1, corresponds to the loss of all acid-adsorbing power.

The initial rate of acid or base adsorption by charcoal from a given solution is great, but the rate decreases rapidly with time. Curve 1 in Fig.

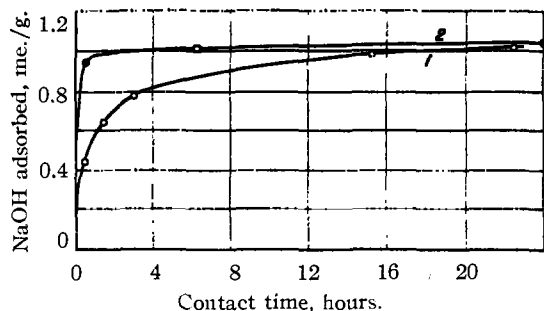


Fig. 3.—Time dependence of sodium hydroxide adsorption: O, granules not crushed, 25°; ●, crushed, 25°; □, crushed, 40°.

3 shows the variation with time of adsorption from 0.03 *N* NaOH solution by a selected preparation, TUC-45. The limiting value of the adsorption is reached (approximately) after about twenty-four hours; the value obtained for the usual half-hour contact period is only a fraction (~50%) of this final value. Experiments were performed to determine whether the slowness of the uptake is due to a slow adsorption at the charcoal surface or to the time required for the solution to diffuse to the inner surface of the charcoal granules through the fine pores of the adsorbent. That the latter is the prime factor is shown by Curve 2, Fig. 3, which shows that the same final adsorption value is reached more rapidly when the charcoal is ground (before adsorption but after oxygen treatment) to pass through a no. 60 screen (24 meshes per cm.). On Curve 2 is also plotted a point for adsorption at 40° by the same charcoal (ground to facilitate rapid adsorption). From the fact that this point falls on the curve representing the behavior of the ground charcoal at 25°, we may conclude that a temperature variation of about 15° does not appreciably affect the final adsorption values. Other experiments with unground charcoal at 40°, however, indicate that the higher temperature does increase the *rate* at which the final value is reached. It would be possible to determine diffusion constants and the activation energy for the diffusion from similar experiments with carefully sized particles; this was not done, however.

The dependence of adsorption of base upon concentration of solution is shown in Fig. 4. The adsorption data plotted are the "final" or equilibrium values, *i. e.*, those observed after at least twenty-four hours of immersion. The ordinates of the three isotherms for the treated materials appear to approach limiting values as the concentration is increased; these three curves can be closely represented by the familiar Langmuir equation.

The adsorption was determined, as stated previously, from the change in concentration of the sodium hydroxide solution. When the solutions were concentrated, the adsorption was measured by the difference between two large and nearly equal concentrations. The points at the extreme

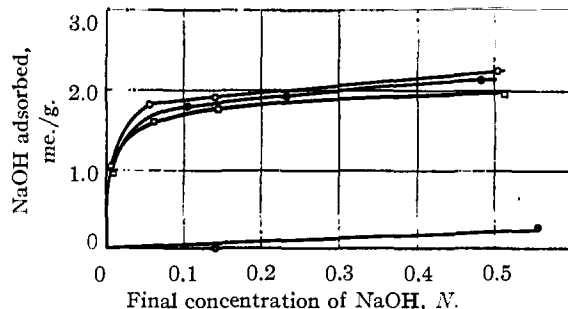


Fig. 4.—Sodium hydroxide adsorption isotherms: O, N-19 TUC-60; ●, N-19 TUC-45; □, N-19 TUC-55; ●, N-19.

right of the figure are, therefore, relatively inaccurate; it is possible that the base adsorbed at high concentrations by untreated CWS N-19 is less than the experimental error, and it may be zero.

No detailed quantitative investigation of hydrochloric acid isotherms on untreated materials was made; such studies have been reported by Bruns and Frumkin¹⁶ and Burstein, Frumkin and Lawrowskaja.⁷

The ratio of the gram atoms of oxygen in a charcoal to the maximum moles of base adsorbed is of interest. Sample TUC-45, for example, which contains 12.7% oxygen (Table III), can adsorb about 2.2 me. of sodium hydroxide per g. For this sample, therefore, 3.6 g. atoms of oxygen are required for the adsorption of one mole of base. An almost identical value (3.7 g. atoms/mole) may be calculated for sample TUC-60. This value of the ratio does not lend itself to simple interpretation and will not be discussed here.

For a few samples adsorption values were determined for relatively high concentrations (0.5 *N*) of acid and base, and for "infinite" of contact between solution and sample (twenty-four hours or more). These data have been plotted in Fig. 5, which for theoretical purposes is of more significance than is Fig. 1. The slope of the line indicates that for every equivalent of acid-adsorbing power lost by CWS N-19 four to five equivalents of base-adsorbing power are gained. Again this figure is not easily interpreted.

The acid-base adsorption properties of oxygen-treated materials seem to be stable toward moder-

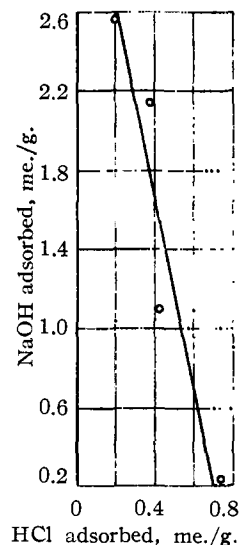


Fig. 5.—Adsorption of acid and base from solution: 0.5 *N* solutions, "infinite" contact times.

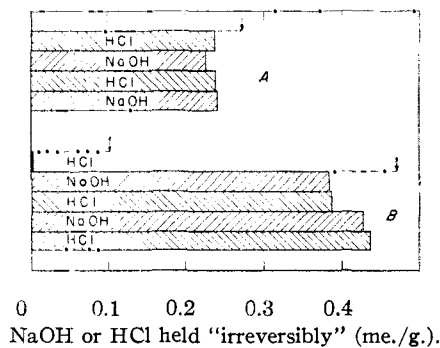


Fig. 6.—“Irreversible” adsorption of sodium hydroxide and hydrogen chloride: A, N-19; B, N-19 TUC-40.

ate aging conditions. The acid- and net base-adsorbing power of one sample was unchanged during (dry) storage for over three months in a stoppered bottle. For another sample (TUC-86, Table II), no change was produced by a twenty-four-hour period of evacuation at 400°.

Nature of the Adsorption from Solution.—

The adsorption data discussed above were obtained from the concentrations of hydrogen or hydroxyl ion in the solution before and after contact with the charcoal. This type of measurement gives no information regarding either (a) the extent of reversibility of the adsorption, or (b) the extent to which Cl^- is simultaneously adsorbed with H^+ , or Na^+ with OH^- . Both questions were studied.

Attempts were made to wash out adsorbed material with water at room temperature. In most experiments a rather sharp distinction could be made between reversibly and irreversibly adsorbed material. One gram of ordinary CWS N-19, for example, adsorbed 0.27 me. of 0.03 *N* HCl solution. After it had been washed for two days, it retained 0.246 me. of hydrochloric acid, *ca.* 90% of the amount originally adsorbed. Further washing over a six-day period removed only 0.002 me. In this case we may say that 0.24 me. of hydrochloric acid is “irreversibly” adsorbed by a gram of charcoal.

The original amount, 0.27 me., and irreversible adsorption, 0.24 me., are represented in Fig. 6 by the arrow and the first bar, respectively. When the hydrochloric acid-treated and washed sample of CWS N-19 was subsequently immersed in sodium hydroxide solution at room temperature and again washed, 0.23 me. (an amount which differs from 0.24 by no more than experimental uncertainty) of sodium hydroxide was neutralized (see Fig. 6A, bar 2), whereas the original CWS N-19 neutralized no sodium hydroxide. This cycle can be repeated, *i. e.*, the sample can again be made to adsorb hydrochloric acid (Fig. 6A, line 3) and subsequently to neutralize sodium hydroxide (Fig. 6A, line 4).¹⁷

(17) Somewhat similar experiments were made by Miller (*J. phys. Chem.*, **36**, 2967 (1932)), who showed that hydrochloric acid adsorbed by charcoal is incompletely removed by washing with

The first arrow of Fig. 6B represents the original acid adsorption (after a one-half hour contact period) of TUC-40, a typical oxygen-treated sample (Table I). TUC-40 did not adsorb any hydrochloric acid “irreversibly,” as indicated by a bar of zero length. When this charcoal was subsequently immersed in an 0.03 *N* sodium hydroxide solution (for one-half hour), its original adsorption was 0.47 me. of sodium hydroxide solution per gram (indicated by the second arrow of Fig. 6B). The “irreversible” adsorption (Fig. 6B, line 2), determined after a series of washings, was 0.37 me. of sodium hydroxide per g., or about 75% of the original adsorption. When this base-containing charcoal was immersed in 0.03 *N* hydrochloric acid it neutralized 0.38 me. of hydrochloric acid (Fig. 6B, bar 3). Successive immersions in sodium hydroxide and hydrochloric acid solutions showed that the cycle could be repeated (bars 4 and 5).

After each pair of immersions, represented in Fig. 6A or Fig. 6B, a mole of sodium chloride is formed per mole of acid or base adsorbed. Inasmuch as the charcoals do not adsorb appreciable quantities of sodium hydroxide from aqueous solution, it seemed likely that the salt formed would be liberated by the charcoal to the aqueous phase. That this was true was shown by two methods for CWS N-19: (1) No increase in ash content of N-19 resulted from adsorption of hydrochloric acid followed by adsorption of sodium hydroxide; and (2) an analysis of the sodium hydroxide solution showed that the immersion of the charcoal containing hydrochloric acid had produced no change in the sodium concentration.¹⁸ A similar analysis of the hydrochloric acid solution after TUC-40 had been immersed in it (Fig. 6B) showed that one equivalent of sodium had been released for each equivalent of sodium hydroxide adsorbed from the preceding solution. It is apparent that each complete cycle leaves the charcoal in essentially its original condition, and that the adsorptions of base and acid in turn could be repeated many times.

The removal from solution of a certain amount of OH^- when an oxygen-treated charcoal is immersed in sodium hydroxide may imply, but does not prove, that the same number of moles of Na^+ is also removed; desorption of some acid liberated by the charcoal could reduce the OH^- concentration (by neutralization) without decreasing the Na^+ concentration. In a series of experiments the nature of the base adsorption by TUC-55 (Table I) was investigated. Analysis of the sodium content of the solution revealed that Na^+ and OH^- are indeed removed in equivalent quantities.¹⁹

water, and that the residual hydrochloric acid is removed by treatment with boiling sodium hydroxide solution.

(18) The sodium content of the solution was determined from the weight of sodium sulfate residue resulting from treatment with excess sulfuric acid and evaporation to dryness.

(19) Analogous experiments by King (ref. 8) have shown that certain charcoals prepared from pure sugar remove the two ions, H^+ and Cl^- , in equivalent amounts on immersion in hydrochloric solution. Untreated N-19 was found to behave in identical fashion.

These experiments still leave unanswered the question of whether the OH^- itself is adsorbed directly by the charcoal or whether it is neutralized by H^+ liberated (when Na^+ exchanges places with it) from the charcoal, *i. e.*, when H^+ is released by an $\text{Na}^+ - \text{H}^+$ exchange. In these experiments these two processes are indistinguishable. We shall simply follow the usual custom and adopt the word "adsorption" to describe both ion exchange and simple adsorption.

Outgassing.—Several investigators have reported that changes produced by activation are reversed by outgassing at higher temperatures ($850\text{--}950^\circ$) and subsequent exposure to air.^{14,11} Table II contains the results of a number of such experiments. The acid- and base-adsorptive properties of untreated CWS N-19 were changed very little by outgassing (treatment in vacuum) at 900° , but the acid-adsorbing power of all the oxygen-treated products of N-19 was increased and the base-adsorbing power decreased. Sufficiently vigorous treatment produced an acid-adsorbing power greater than that of the original material, which is probably due to an increase in surface area (see below) during oxygen treatment.

Ultimate Analyses and Heats of Combustion.—Analyses for carbon, hydrogen, ash and oxygen (the oxygen by difference) were made for a number of the samples. These results, together with the heats of combustion for the same samples are listed in Table III. Data for a sample of very pure graphite²⁰ are included. In general, duplicate analyses agreed within 0.3% for carbon and within 0.08% for hydrogen. All the values given are averages of at least two determinations. One sample, TUC-46, contains 18.3% oxygen; in this charcoal, therefore, there is one oxygen for each 5.95 carbon atoms.

Oxygen treatment has no large effect on the hydrogen content of the charcoal, although outgassing at high temperatures reduces it somewhat.²¹ (The high ash content of TUC-41 indicates that the sample may have been contaminated, and the results for TUC-41 ought to be somewhat discounted.) Furthermore, the per cent. ash increases somewhat during oxygen treatment as is to be expected if some of the ash from the charcoal burned away remains with the granule.²²

From the respective heats of combustion of a pair of samples containing sufficiently different amounts of oxygen, it is possible to calculate the heat of adsorption of oxygen on (or heat of combination with) charcoal. For simplicity we have used the difference between the heat of combustion of each sample containing more than 10% oxygen and the heat of combustion of the hypothetical material determined from an extrapolation of the

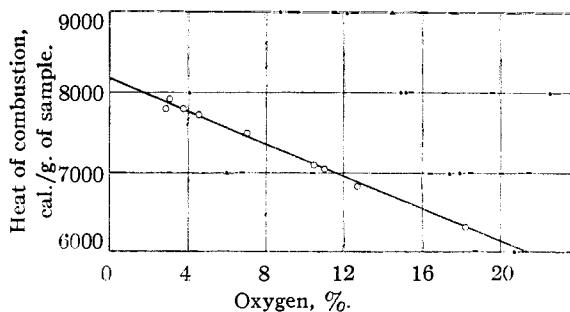


Fig. 7.—Dependence of heat of combustion on oxygen content.

curve in Fig. 7 to zero oxygen content, *i. e.*, 8160 calories per gram. The method may be illustrated with the calculation for TUC-46: Sufficient TUC-46 to contain 1 g. of oxygen weighs 5.46 g. The heat liberated by the combustion of 5.46 g. is 34,600 calories. Neglecting the hydrogen and ash content of the sample, we may, without serious error, treat it as containing 4.46 g. of carbon. The heat liberated by the combustion of 4.46 g. of hypothetical oxygen-free material is $8160 \times 4.46 = 36,400$ calories. The difference, 1800 calories, is the liberation of heat accompanying the adsorption of one gram of oxygen on the oxygen-free charcoal. The mean of four values is 1890 calories per gram of oxygen, *i. e.*, 60,000 calories per mole of oxygen. An alternative calculation, based upon the assumption that hydrogen contributes to the heat of combustion 34,200 calories per gram (the heat of combustion of pure hydrogen) and that ash contributes nothing to the heat of combustion, yields a value of about 65,000 calories per mole of oxygen. Since the heats of formation of hydrocarbons per gram of hydrogen are small in comparison with 34,200, the true value is probably close to 65,000 calories per mole of oxygen adsorbed by (or combined with) the charcoal.

It is instructive to compare this value with previous measurements of the heats of adsorption of oxygen on charcoal. Keyes and Marshall,²³ using an ice calorimeter, observed the liberation of 70,000 calories per mole of oxygen adsorbed on clean charcoal at 0° , but found that the heat of adsorption decreased to 4,000 calories per mole of oxygen as the amount of adsorbed oxygen increased. Blench and Garner²⁴ reported heats of adsorption of about 60,000 calories per mole of oxygen for room temperature and much larger values at 450° ; but their experimental method, for reasons pointed out by Schwab,²⁵ seems unreliable. More recently Marshall and MacInnes²⁶ have observed heats of adsorption as large as 129,000 calories per mole for oxygen at extremely low pressures and as small as 72,000 calories per g. when only 6 micromoles of oxygen per gram of

(20) The graphite sample was obtained through the courtesy of Dr. George Boyd.

(21) Cf. Lowry, *THIS JOURNAL*, **46**, 824 (1924).

(22) More accurate determinations with preparations from a different charcoal indicate that the increase in ash content is not as great as it would be if all the ash were retained by the granule.

(23) Keyes and Marshall, *THIS JOURNAL*, **49**, 156 (1927).

(24) Blench and Garner, *J. Chem. Soc.*, 1288 (1924).

(25) Schwab, "Catalysis," D. Van Nostrand Co., New York, N. Y., 1937, p. 200.

(26) Marshall and MacInnes, *Can. J. Research*, **15B**, 75 (1937).

charcoal had been adsorbed. All these results are in agreement with the conclusion that the heat of adsorption at room temperature decreases with increase in the amount of oxygen adsorbed. By contrast, our calculations and the straight line of Fig. 7 showed that at 400° the heat of adsorption (or combination) is nearly constant over the range of composition investigated. Noteworthy, the value of 65,000 calories per mole of oxygen is of the same order of magnitude as the heats of reaction between graphite and one mole of oxygen to form one mole of gaseous carbon dioxide (94,200 calories) or two moles of gaseous carbon monoxide (53,200 calories).

Surface Areas and Gas Adsorption.—Dr. P. H. Emmett has determined nitrogen, ammonia, hydrogen chloride and water isotherms on a number of the oxygen preparations. These results are reported in detail by him elsewhere,²⁷ and only a summary of the conclusions will be presented here.

Values of the surface areas of several samples, determined by the nitrogen adsorption method,²⁸ are listed in Table IV. Extensive oxygen treatment at 400° results in a significant increase in surface area. Outgassing at 900°, on the other hand, has but a small effect on the area per gram of sample, of either N-19 or its oxygenated product, TUC-45. Since TUC-50 contains more carbon per gram of sample than does TUC-45, this fact indicates that the outgassing is accompanied by an appreciable sintering of the residual carbon.

The hydrogen chloride adsorption at high gas pressures is increased by oxygen treatment, the increase being roughly proportional to the increase in surface area. At low pressures of hydrogen chloride no appreciable enhancement of adsorption occurs.

At high ammonia pressures the adsorption of ammonia seems also to be determined chiefly by the surface area and pore volume of the charcoal. The ammonia adsorption at low pressures is greatly increased by oxygen treatment, however; in contrast to untreated N-19, the oxygen-treated materials adsorb considerable ammonia even at the lowest pressures investigated. This is in qualitative agreement with the increase in base-adsorbing power caused by oxygen treatment (see above), but insufficient data are available to establish a quantitative relation. Outgassing at 900° destroys the ability to adsorb large quantities of ammonia at low pressure.

The adsorption of water is also enhanced by treatment with oxygen. In addition to a general rise in the high pressure portion of the isotherm (corresponding to the increase in nitrogen adsorption), there is a greatly increased adsorption at low relative pressures, presumably due to the same factors which increase the ammonia adsorption. At a relative pressure of 0.50, for example,

(27) Emmett, *Chem. Revs.*, **43**, 69 (1948).

(28) Brunauer, Emmett and Teller, *This Journal*, **60**, 309 (1938).

TUC-46 can adsorb an amount of water ten times greater than that adsorbable by untreated N-19.²⁹

Summary

Treatment of a low-ash charcoal with oxygen at 400° increases the ability of the charcoal to remove alkali from solution and decreases its ability to remove acid. The amount of acid or base removed by a charcoal increases with time of immersion, presumably because of the time required for diffusion through the pore system of the charcoal, and eventually approaches a limiting value. The rate of adsorption but not the limiting value is increased by a rise of temperature from 25 to 40° or by the grinding of the material to pass a no. 60 mesh screen. The limiting value is itself a function of concentration and approaches a limit as concentration is increased.

Most of the hydrochloric acid adsorbed from solution by an untreated charcoal is not readily extracted with water, but it can be removed by treatment with a solution of sodium hydroxide. The chloride content of the extracting solution is increased during the process and the hydroxyl ion content decreased, while the sodium ion concentration remains essentially constant. After the alkali treatment the charcoal is able to adsorb acid from aqueous solution.

A similar (but converse) series of experiments can be performed with a base-adsorbing, *i. e.*, oxygen-treated, charcoal; the firmly held sodium hydroxide can be removed by extraction with hydrochloric acid solution, leaving the material in condition again to adsorb sodium hydroxide.

Both Na⁺ and OH⁻ are removed from solution by a base-adsorbing charcoal. Similarly, both H⁺ and Cl⁻ are removed by an acid-adsorbing material.

The stability of the oxygen complex formed by oxygen treatment at 400° is indicated by its heat of formation; about 65,000 calories are evolved per mole of oxygen combining with the charcoal.

The high temperature outgassing of a treated charcoal reverses the changes in acid- and base-adsorptive properties produced by treatment with oxygen. When the oxygen is pumped off (as carbon dioxide, etc.), the volume of the charcoal decreases correspondingly, so that the apparent density changes very little.

Oxygen treatment increases the surface area of a charcoal, and there is a concomitant increase in the ability to adsorb gaseous hydrochloric acid, ammonia, and water at high relative pressures. In addition, there is a striking increase in the adsorption of water and ammonia at low pressures.

CHICAGO, ILLINOIS

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(29) The increased affinity of charcoal for water is revealed also by the ease with which the oxidized material is wetted by water. Most ordinary, unoxidized charcoals float for several minutes, some for hours, on the surface of water. A material containing even a small amount of the complex settles within a few seconds, and a highly oxidized material drops through the water surface at once. Also, cf. Miller, *ref. 17*.