[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Alteration of Adsorption Properties of Charcoal: Activation of Charcoal in Different Gases at Different Temperatures

BY F. E. BARTELL AND LEWIS E. LLOYD

Three types of activated charcoal were prepared in this investigation, a "High Temperature Charcoal," activated at 1000° in an oxidizing atmosphere, a "Medium Temperature Charcoal," activated with oxygen at 400°, and a "Low Temperature Charcoal," activated below 250° in a strongly oxidizing gaseous atmosphere. For these charcoals, the following properties were determined: preferential adsorption of benzene–ethanol solutions, acid–base adsorption, and the sign of the particle charge of the charcoals.

Experimental

The ash-free sugar charcoal used in this investigation was prepared by charring recrystallized sucrose. After a preliminary grinding, the charred material was heated in nitrogen for two hours at 950°. It was then purified according to Miller;[1] and after the final heating in nitrogen at 950°, only that portion was used which passed a 300 mesh sieve but did not pass a 350 mesh sieve. The charcoal was stored in a wide-mouthed, screw-cap bottle until used. This charcoal will subsequently be referred to as "stock" charcoal.

The charcoal was activated in a quartz tube which was held in a horizontal position and could be rotated to give more complete mixing of the charcoal and activating gas. The quartz tube was heated by an electric furnace which could be removed from the tube by merely sliding it. This made it possible to cool the charcoal quickly at the end of an activation treatment. In all cases the charcoal was cooled in an atmosphere of the same gas as that used for the activation.

Preferential Adsorption Experiments.—The preferential adsorption which the different types of activated charcoal gave in benzene–ethanol solutions was determined by the interferometric method developed by Bartell and Sloan.[2] The method consists in placing a known amount of the adsorbent in each of several different concentrations of solutions of a pair of suitable liquids, and determining the change in fractional concentration of each solution by means of the interferometer. The data are plotted in terms of the $H\Delta x/m$ value against the mole fractional concentration of ethanol (x), where H is the number of milliequivalents of solution, Δx the change in fractional concentration, and m the weight of adsorbent. The $H\Delta x/m$ value is calculated from the data by the method of Bartell and Sloan.[2]

When the data are plotted in the manner described, an S-shaped curve is obtained. The point at which this S-shaped curve intersects the x-axis will be designated as the X_0 value. The X_0 value gives the maximum concentration at which ethanol is preferentially adsorbed, and since the concentration is given in mole fractions of ethanol, the X_0 value also gives the fraction of the entire concentration range (in molar units) over which ethanol is preferentially adsorbed. Those solids which adsorb polar ethanol over a major portion of the entire concentration range are less organophilic and more hydrophilic than solids which adsorb non-polar benzene over a major portion of the entire range. The X_0 value found by Bartell and Sloan[2] for organophilic charcoal with benzene–ethanol was 0.200. The X_0 value found by Bartell, Sloan, and Scheffler[3] for hydrophilic silica with benzene–ethanol was 0.850. The X_0 value gives, then, a comparative measure of the organophilic or hydrophilic nature of the solid; the higher the X_0 value, the more hydrophilic the solid. As yet no point has been established on the concentration axis dividing organophilic solids from hydrophilic solids. It is possible that such a point may be established by further experimentation.

"High Temperature Charcoal."—In order to make a comparison with the benzene–ethanol preferential adsorption curve of Bartell and Sloan[2] and to make measurements of other properties of a charcoal similar to that which they used, some charcoal was activated at 1000° in a slow stream of oxygen. The oxygen was passed through at the rate of 200 cc. per hour for seven and one-half hours. The S-shaped curve (see Fig. 1) obtained with this charcoal (Charcoal 1) crossed the x-axis at a value of 0.210 mole fraction of ethanol as compared to the 0.200 value obtained by Bartell and Sloan.[2] Their charcoal was activated in a stream of air, but, as was to be expected, air and oxygen gave about the same activation of charcoal at 1000°.

To avoid possible activation effects with oxygen over a temperature range during cooling, carbon dioxide was used as the activating gas in subsequent high temperature treatments. Charcoal 2 was activated for two hours in oxygen at 1000° and then for two hours in carbon dioxide at the same temperature. Charcoals 3 and 4 were activated in carbon dioxide at 1000° for five hours. The S-shaped curves for Charcoals 2, 3, and 4 are given in Fig. 1. The X_0 value for the preferential adsorption was shifted from 0.210 for Charcoal 1, which was cooled in oxygen, to 0.125 for Charcoals 3 and 4, which were cooled in carbon dioxide. The experimental data obtained for Charcoal 4, a typical "High Temperature Charcoal," are given in Table I.

The fact that the charcoals which were activated and cooled in carbon dioxide gave a lower X_0 value than the X_0 value of charcoal which was activated and cooled in air or oxygen indicates that during the process of cooling in oxygen some of the charcoal surface had been changed from the "High Temperature Charcoal" type. The

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[1] E. J. Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

[2] F. E. Bartell and C. K. Sloan, THIS JOURNAL, **51**, 1637 (1929).

[3] F. E. Bartell, G. Scheffler and C. K. Sloan, *ibid.*, **53**, 2501 (1931).

TABLE I

CHARCOAL No. 4

N = Weight of solution; m = weight of adsorbent; dR = change in scale division on interferometer; c = weight fraction of solute; x = mole fraction of solute; H = total number of millimoles of solution. For method of calculating $H\Delta x/m$, see Bartell and Sloan.[2]

N	m	dR	dc/dR $\times 10^{-5}$	c	x	$H\Delta x/m$
4.3472	0.2387	37.4	1.860	0.012038	0.020235	0.2488
4.3352	.2449	38.1	1.875	.027325	.045452	.2697
4.3255	.2419	20.7	1.900	.051115	.083666	.1475
4.3029	.2388	− 16.9	1.937	.094684	.15057	− .1202
4.2571	.2340	− 77.6	2.020	.18356	.27592	− .5491
4.1702	.2400	−211.7	2.188	.37107	.50000	−1.3688
4.0337	.2402	−345.0	2.420	.60784	.72430	−2.1414
4.0008	.2379	−349.2	2.552	.83565	.84955	−2.1189
3.9556	.2372	−304.5	2.659	.86289	.91429	−1.7766
3.9287	.2382	−240.6	2.720	.92522	.95449	−1.4658
3.9071	.2352	−137.7	2.772	.97915	.98760	−0.8196

"1000° Charcoals" cited in the literature undoubtedly represent various degrees of completeness of 1000° activation, and although their properties are fairly similar, further experiment may show that the term "1000° Charcoal" lacks sufficient specificity to warrant this definite designation.

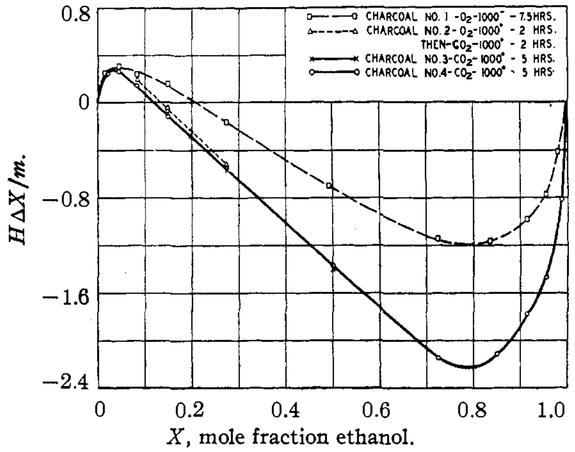

Fig. 1.—Preferential adsorption: Charcoal activated at 1000° in oxidizing atmosphere.

The concept that adsorption occurs at definite activated spots, which are probably unit cells at the crystal surface, has been accepted generally in explaining adsorption phenomena. According to this concept, an adsorbent becomes activated by having each of the spots or units of the surface changed into what constitutes the activated state. Thus, a "High Temperature Charcoal" would be one whose surface had all the unit spaces activated to that type. In actual practice complete activation of one type is probably never attained but may be approached. The exact properties of a given charcoal will depend both on the type of activation and also on the relative proportion of the surface which has the desired activation.

The "High Temperature Charcoal" was found to be quite stable at temperatures up to 150°. Part of the charcoal activated with and cooled in an atmosphere of carbon dioxide, when placed back in the activating tube and treated with dry oxygen for two hours at 150°, showed no change in X_0 value. The curve for the charcoal after this treatment was practically coincident with the one which the 1000° treatment gave.

"Medium Temperature Charcoal."—The first "Medium Temperature Charcoal" prepared during this investigation (Charcoal 5) was taken from the "stock" supply and activated directly at 400° in oxygen for seven and one-half hours without previous activation at 1000°. The preferential adsorption curve for Charcoal 5 is given in Fig. 2.

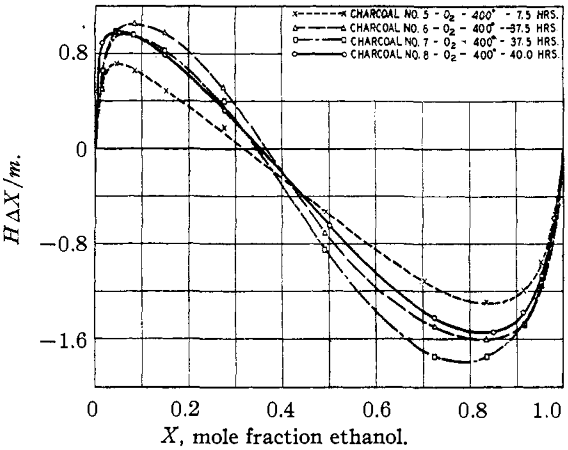

Fig. 2.—Preferential adsorption: Charcoal activated at 400° in oxygen.

This charcoal approached the characteristics which were expected except that the X_0 value, 0.315, was not so high as was expected in view of the fact that it had been predicted by other workers[4] that this charcoal would be hydrophilic. In the next two runs (Charcoals 6 and 7) the charcoal was first activated at 1000° in oxygen for seven and one-half hours and then for thirty-seven and one-half hours at 400° in oxygen. Charcoal 8 was first activated for five hours at 1000° in carbon dioxide and then in oxygen at 400°. The properties of Charcoals 6, 7, and 8 were quite similar to those of Charcoal 5. The preferential adsorption curves for Charcoals 6, 7, and 8 are shown in Fig. 2, and the experimental data for Charcoal 8 are given in Table II. The X_0 values for Charcoals 6, 7, and 8 are

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(4) I. M. Kolthoff, THIS JOURNAL, 54, 4473 (1932).

Table II

Charcoal No. 8

N	m	dR	$dc/dR \times 10^{-5}$	c	x	$H\Delta x/m$
4.3471	0.2455	125.7	1.860	0.012038	0.020235	0.8917
4.3364	.2446	138.1	1.875	.027325	.045452	.9789
4.3236	.2456	135.8	1.900	.051115	.083666	.9532
4.2974	.2487	109.0	1.937	.094684	.15057	.7968
4.2542	.2454	47.6	2.020	.18356	.27592	.3211
4.1740	.2474	− 99.3	2.188	.37107	.50000	− .6327
4.0669	.2460	−232.5	2.420	.60784	.72430	−1.4203
3.9979	.2452	−261.3	2.552	.83565	.84955	−1.5374
3.9550	.2461	−237.6	2.659	.86289	.91429	−1.3783
3.9246	.2471	−187.4	2.720	.92522	.95449	−1.0705
3.9020	.2468	−103.0	2.772	.97915	.97915	−0.5833

very similar, the range being from 0.346 to 0.370. The X_0 value for Charcoal 5 is a little lower, being only 0.315. This difference in X_0 values is probably due to differences in the completeness of the medium temperature activation. As was suggested for the term *1000° Charcoal*, the term *400° Charcoal*, which also appears in the literature, may in the future be shown to lack the previously implied specificity.

A small change in the X_0 value of "Medium Temperature Charcoal" is effected by subsequent low temperature treatment. Some charcoal of this type was heated in oxygen at 125° for forty hours. The X_0 value was found to have been reduced by 0.013 unit. The charcoal was then further treated with oxygen (saturated with water vapor at 25°) at 150° for another forty hours. The X_0 value was reduced by 0.014 unit. The "Medium Temperature Charcoal" was fairly stable, then, since a total low temperature treatment with oxygen for eighty hours changed its X_0 value only by 0.027. At ordinary temperatures "Medium Temperature Charcoal" changes slowly and appears to revert to the "High Temperature Charcoal" type.

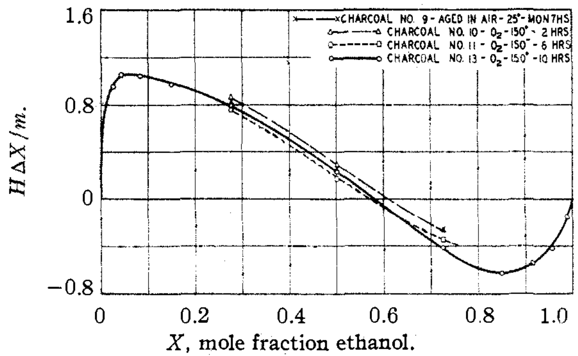

Fig. 3.—Preferential adsorption: Charcoal activated at 150° in oxidizing atmosphere.

"Low-Temperature Charcoal."—Some of our experiments had indicated that the "stock" charcoal had a larger X_0 value, and was more hydrophilic than the "Medium Temperature Charcoal." A special run was made, therefore, to determine the preferential adsorption of the "stock" charcoal. This untreated "stock" charcoal, No. 9, gave an X_0 value of 0.610, which is considerably higher than 0.370, the highest X_0 value for the "Medium Temperature Charcoal." The curve for Charcoal 9 is shown in Fig. 3. The "stock" charcoal was then heated in oxygen at 150° to see if such a low temperature oxidation would produce a more hydrophilic charcoal. Runs at 150° for two hours (Charcoal 10), six hours (Charcoal 11), and for ten hours (Charcoal 12) were made. The curves for these charcoals are given in Fig. 3. A low temperature treatment of the "stock" charcoal in oxygen for ten hours reduced the X_0 value from 0.610 to 0.580, and thus the "stock" charcoal, like the "Medium Temperature Charcoal," is changed slightly by a low temperature oxygen treatment and appears to revert toward a higher temperature type.

Some preliminary preferential adsorption runs on the "stock" charcoal just after it had been prepared and heated at 950° in nitrogen showed that at the time it was prepared the charcoal was organophilic, that is, it preferentially adsorbed benzene over the greater portion of the concentration range. The results on low temperature oxygen treatment of the "stock" charcoal and the "Medium Temperature Charcoal" show that oxygen alone would not be expected to change the "stock" charcoal from its original organophilic to a hydrophilic nature. It appeared that a catalytic effect must have brought about some type of activation during the time that the charcoal stood after its preparation. Oxides of nitrogen are known to be effective catalysts for oxidation reactions. Bartell and Bristol[5] found that traces of nitric oxide added to the oxygen stream greatly increased the oxidizing action on stibnite mirrors even at relatively low temperatures. It seems probable that traces of oxides of nitrogen were formed when the charcoal was heated and cooled in nitrogen during its preparation. Oxygen which is adsorbed on the surface of charcoal is known to be very difficult to remove, its complete removal requiring extreme outgassing.[6,7] Some of the oxygen which was adsorbed on the charcoal before the nitrogen treatment probably reacted with nitrogen during the 950° treatment and formed oxides of nitrogen. It seemed possible that traces of the oxides might have remained on the "stock" charcoal as it cooled, and catalyzed a slow oxidation at 25° as the "stock" charcoal stood in its container.

To test the above theory, some activation treatments were tried using strongly oxidizing gaseous mixtures at low temperatures. These treatments increased the X_0 values of the charcoals. Some "Medium Temperature Char-

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[5] F. E. Bartell and K. E. Bristol, unpublished.

[6] Irving Langmuir, This Journal, **37**, 1154 (1915).

[7] A. Frumkin, R. Burstein and P. Lewis, *Z. physik. Chem.*, **157** 445 (1931).

TABLE III

CHARCOAL NO. 14

N	m	dR	dc/dR × 10^{-5}	c	x	$H\Delta x/m$
4.2590	0.2317	174.0	2.020	0.18498	0.27781	1.3179
4.1710	.2303	94.1	2.188	.37072	.49963	0.6439
4.0625	.2313	− 8.0	2.420	.60756	.72406	− .0520

coal" (with an X_0 value of approximately 0.370) was treated with a mixture of nitric oxide, oxygen, and water vapor at 150° for ten hours. The resulting product, Charcoal 13, was found to have an X_0 value of 0.545 and had, therefore, been made considerably more hydrophilic.

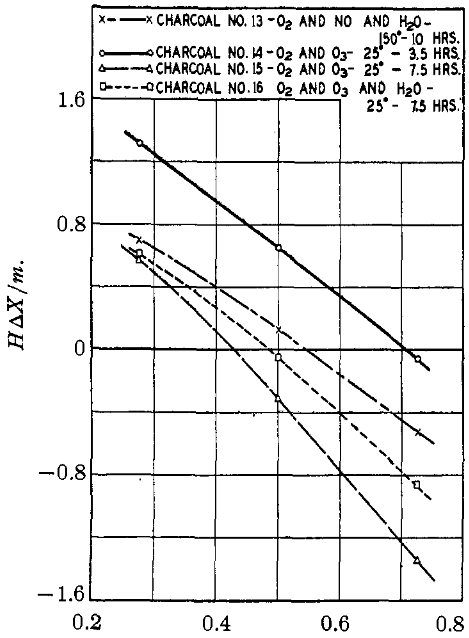

Fig. 4.—Preferential adsorption on charcoal activated at low temperature in oxidizing atmosphere.

Several runs were next made (Charcoals 14, 15, and 16) using ozone as oxidizing gas. Ozone, a fairly strong oxidizing agent, has the advantage that no foreign material other than that already used in the oxygen treatments, is exposed to the charcoal surface. The ozone was generated by a silent discharge apparatus which furnishes from 8 to 10% of ozone. In two of the runs, water vapor was excluded (Charcoals 14 and 15), and in one it was added (Charcoal 16). The starting material for Charcoal 14 was "stock" charcoal, and for Charcoals 15 and 16, it was "Medium Temperature Charcoal." In every case the charcoal thus treated was made more hydrophilic, that is, its X_0 value was increased. In the run in which the "stock" charcoal was treated with ozone (Charcoal 14), its X_0 value was increased from about 0.610 to 0.710. Nitric oxide produced greater effects than ozone, and had "stock" charcoal been activated with nitric oxide and oxygen as was the "Medium Temperature Charcoal" for Charcoal 13, and had the activation been continued for a sufficient period of time, it is possible that a charcoal with preferential adsorption properties approaching those of silica (X_0 = 0.850) might have been prepared. The curves for Charcoals 13, 14, 15, and 16 are given in Fig. 4. Experimental data for Charcoal 14 are given in Table III.

A graph showing the change in the preferential adsorption caused by different activation treatments of charcoal is shown in Fig. 5. (The data for these curves are given in Tables I–III.) On this graph is plotted also the curve for silica as given by Bartell, Sloan, and Scheffler.[8] The X_0 value for the most organophilic charcoal (Charcoal No. 3) is 0.125, while the X_0 value for silica, a very hydrophilic solid, is 0.850. The X_0 value of 0.125, which was found to be quite reproducible for charcoal heated in carbon dioxide at 1000°, appears to be characteristic of the "High Temperature Charcoal." A representative "Medium Temperature Charcoal" curve is given in Fig. 5 and is labeled "M. T. Charcoal." An X_0 value in the range of 0.350 to 0.370 is probably characteristic of the "Medium Temperature Charcoal." This indicates that "Medium Temperature Charcoal" preferentially adsorbs ethanol over a larger

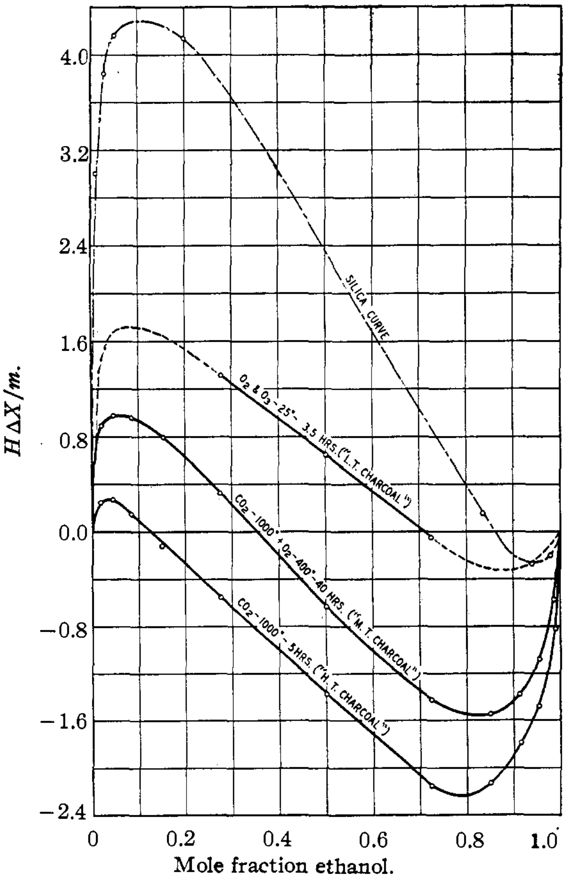

Fig. 5.—Comparison of different charcoals: preferential adsorption of ethanol from benzene.

TABLE IV

PROPERTIES OF DIFFERENT ACTIVATED CHARCOALS

	Activation treatment								Acid-base ads. (50 cc. soln. 1 g. charcoal) milliequiv./g.	
	Pretreatment			Final treatment						
Charcoal	Gas	Temp., °C.	Time, hrs.	Gas	Temp., °C.	Time, hrs.	x_0	Charge on particle	HCl	NaOH
1				O_2	1000	7.5	0.210	(+) + (−)	0.172	0.000
2				$O_2 + CO_2$	1000	2 ea.	.136	(+) + (−)	.260	.030
3				CO_2	1000	5	.125	(+) + (−)	.281	.000
4				CO_2	1000	5	.125	(+) + (−)	.303	.000
5				O_2	400	7.5	.315	(−)	.029	.395
6	O_2	1000	7.5	O_2	400	37.5	.370	(−)	.000	.468
7	O_2	1000	7.5	O_2	400	37.5	.346	(−)	.002	.462
8	CO_2	1000	5	O_2	400	40	.348	(−)	.000	.462
9	Stock charcoal			Untreated			.610	(−)		
10				O_2	150	2	.615	(−)		
11				O_2	150	6	.575	(−)		
12				O_2	150	10	.580	(−)	.102	.048
13	O_2	400		$O_2 + NO + H_2O$	150	10	.545	(−)		
14	Stock charcoal			$O_2 + O_3$	25	3.5	.710	(−)	.047	.066
15	O_2	400		$O_2 + O_3$	25	7.5	.420	(−)	.030	.889
16	O_2	400		$O_2 + O_3 + H_2O$	25	7.5	.485	(−)	.016	.940

portion of the concentration range than does "High Temperature Charcoal" and is less organophilic, *i. e.*, is more hydrophilic than the latter. A "Low Temperature Charcoal" curve, labeled "L. T. Charcoal," is also given in Fig. 5. A consideration of the curves which were obtained for "Low Temperature Charcoals" leads to the conclusion that none of them are characteristic of charcoal fully activated to the "Low Temperature Charcoal" type. Charcoal completely activated to this type would probably more nearly approach silica (X_0 = 0.850) in its preferential adsorption.

The X_0 values were found to be fairly reproducible for a given activation treatment, and, furthermore, the type of charcoal obtained was independent of the treatment given the charcoal before the final activation. This would seem to indicate that some definite surface structure—probably some definite carbon-oxygen complex such as an oxide—is responsible for the different types of activated charcoal.

Acid-Base Adsorption.—In the acid-base adsorption experiments, 0.01 *N* solutions of hydrochloric acid and sodium hydroxide were used. Methyl red was used as indicator. One-gram samples of the activated charcoal were weighed out and placed in dry flasks; to one-half of these flasks was added 50.00 cc. of 0.01 *N* hydrochloric acid, and to the other half, an equal volume of 0.01 *N* sodium hydroxide. Blanks were run with each set of experiments. The solutions stood with intermittent shaking for ten hours. They were then filtered, and 25.00 cc. of the filtrate pipetted off for titration. The blanks were filtered through the same kind of filter paper and titrated in the same manner. To the flasks containing the sodium hydroxide, 25.00 cc. of the 0.01 *N* hydrochloric acid was added directly and the excess back titrated.

The "High Temperature Charcoal," whether activated with oxygen or carbon dioxide, gave acid adsorption but no base adsorption from dilute solutions of strong inorganic acids and bases. A slight base adsorption which was evidenced by Charcoal 2 was undoubtedly due to the fact that there remained some carbon dioxide on the charcoal which was not chemisorbed. Any such carbon dioxide left on the charcoal would form carbonic acid in solution when the charcoal was suspended in water; this carbonic acid would neutralize some of the base during titration. The "Medium Temperature Charcoal" gave base adsorption, and when the activation was quite complete, it gave no evidence of acid adsorption. Several investigators, Bartell and Miller,[8] Schilow and co-workers,[9,10] and Kolthoff,[4] previously have run some experiments on activated charcoal, determining the acid and base adsorption. Their results on acid-base adsorption and those of the present investigation are in full agreement. Since our charcoals were activated to distinct and essentially pure types of charcoal, our data permit the following conclusion: "High Temperature Charcoal" adsorbs strong inorganic acids but not strong inorganic bases from dilute solutions. "Medium Temperature Charcoal" adsorbs strong inorganic bases but not strong inorganic acids from dilute solutions. Charcoal which is not completely activated to either of the above described types of surface would naturally give both acid and base adsorption. The "Low Temperature Charcoal" which we prepared showed some acid adsorption along with considerable base adsorption.

Charge on Particle.—The particle charge of the activated charcoals was determined by direct observation, with a microscope of the direction in which the particles moved when an electrical potential was applied. The apparatus and method is described by Bartell.[11] The "Medium Temperature Charcoal" and "Low Temperature Charcoal" gave only negatively charged particles in suspension. The "High Temperature Charcoal" showed both positive and negative particles when the suspension was first made up. If the observation was made at once, there were more

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(8) F. E. Bartell and E. J. Miller, THIS JOURNAL, **44**, 1866 (1922).

(9) Nikolai Schilow and Konstantin Tschmutow, *Z. physik. Chem.*, **148**, 233 (1930).

(10) Nikolai Schilow, Helene Schatumowakaja, and Konstantin Tschmutow, *ibid.*, **149**, 211 (1930).

(11) F. E. Bartell, "Laboratory Manual of Colloid and Surface Chemistry," Edwards Brothers, Ann Arbor, Mich., 1936, p. 47.

positive particles than negative ones. In a very short time, less than two minutes, only negative particles remained suspended. The positive particles, which could be seen to settle out very rapidly, apparently had all settled out and left only negatively charged particles. Kruyt and DeKadt[12] reported that charcoal activated at 1000° gave positively charged particles, while charcoal activated at 400° gave negatively charged particles. Kolthoff[4] observed the same relation between particle charge and temperature of activation. Frampton and Gortner[13] attempted to prepare positively charged charcoal but did not succeed in doing so; they reported only negatively charged particles for charcoal activated at 1000°. Wiegand[14] reported that lampblack which was collected by being attracted to a negative plate and, therefore, must have had a positive charge, proved to have a negative charge in an aqueous suspension. Further research regarding the charge of "High Temperature Charcoal" will probably clear up this apparent contradiction in the results on the particle charge for such charcoal.

A summary of the data obtained for all the charcoals is given in Table IV.

Summary

1. Preferential adsorption from benzene–ethanol solutions by charcoals activated at different temperatures and in different gases shows that charcoal can be changed from extremely organophilic charcoal to charcoal approaching in adsorptive properties the hydrophilic adsorbent, silica.

2. The characteristic S-shaped preferential adsorption curves for a series of increasingly hydrophilic charcoals have been plotted, and the points where these curves cross the X-axis, the X_0 values, are shown to be a measure of the relative organophilic or hydrophilic nature of the charcoals.

3. The organophilic "high temperature charcoal" (activated at temperatures near 1000°), when suspended in water, gave both positively and negatively charged particles. This charcoal gave acid adsorption but no base adsorption. The less organophilic "medium temperature charcoal" (activated at temperatures near 400°), when suspended in water, gave only negatively charged particles. This charcoal gave base adsorption. The "low temperature charcoal" (activated in a highly oxidizing atmosphere below 150°), approaching in adsorptive properties hydrophilic silica, when suspended in water, gave only negative particles. This charcoal showed both acid and base adsorption.

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[12] H. R. Kruyt and G. S. DeKadt, *Kolloidchem. Beihefte*, **32**, 349 (1931).

[13] V. L. Frampton and R. A. Gortner, *J. Phys. Chem.*, **41**, 567 (1937).

[14] W. B. Wiegand, *Ind. Eng. Chem.*, **29**, 953 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA]

Physical Chemical Properties of *cis*- and *trans*-Decahydronaphthalene[1]

BY W. F. SEYER AND R. D. WALKER

Introduction.—Little is known of the chemical and physical properties of the dicyclic naphthalene hydrocarbons. An extensive investigation of these compounds can be undertaken only after a method has been found for obtaining these two compounds in a high state of purity and in suitable quantities. The wide variation in the physical data of the two isomeric forms as given by Hückel[2] in his summary of the literature dealing with this subject would indicate that in some of the methods of synthesis the two forms were produced simultaneously, but in varying amounts.

It was thought, therefore, that the most practical method of obtaining the two forms in sufficient quantity was to fractionate the commercial decalin.

Fractionating Apparatus.—It was discovered in a series of preliminary trials that reduced pressure must be used. Decomposition took place during distillation at atmospheric pressure even with a column length of only 1 meter. The complete apparatus used is shown in Fig. 1. The diagram is self-explanatory; hence only a few remarks are necessary to describe the mode of operation. By utilizing a magnet controlled receiving unit, stopcocks at this point were eliminated. The reflux was controlled by sealing a fine capillary tube to the head of the rectifying column. The lagged column was packed with No. 18 galvanized jack chain. The still had a capacity of 3000 cc. and was electrically heated. Water at 20° was pumped from a constant temperature bath to the condensers.

The reduced pressure of 10 mm. was maintained by a Cenco vacuum pump. At this pressure it was found that no pressure regulation device was required to keep the height of mercury in the manometer constant. A sulfuric acid manometer in connection with the one above showed variations in pressure of less than 1 mm.

Materials.—Decalin from various sources was used. Material from the Eastman Kodak Co. showed a consider-

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[1] Original manuscript received August 20, 1937.

[2] Hückel, *Ann.*, **441**, 1 (1925).