124. *Studies in Chemisorption on Charcoal. Part X. Hydrolytic Adsorption.*

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The influence of temperature of activation on the hydrolytic and molecular adsorption of salts by pure sugar charcoal has been studied. Curves are given showing how adsorption per unit area varies with temperature of activation. These curves are continuous, and they show that the fundamental difference between high- and low-temperature charcoals is that the former liberate bases from salts whereas the latter liberate acids. Various factors affecting the shape of the curves are discussed, and it is pointed out that the surface oxide theory cannot give a detailed account of the mechanism of hydrolytic adsorption although it does account for the general trend of the results. The results for different salts are in agreement with observations of previous workers that salts of strong acids and weak bases or strong bases and weak acids are adsorbed both hydrolytically and molecularly, but salts of strong acids and strong bases are adsorbed only hydrolytically.

It has been known for a considerable time that salts are sometimes hydrolytically adsorbed from aqueous solution by activated charcoal. If, for example, a charcoal activated at a high temperature is placed in a solution of a neutral salt, some of the acid formed by the hydrolysis of the salt is preferentially adsorbed and an equivalent amount of free alkali is left in solution. Thus even a salt formed from a strong acid and strong base may be completely hydrolysed by removal of one of the hydrolysis products by adsorption. Much of the early work on the subject was carried out on impure charcoals, and the results are, on the whole, inconclusive and often contradictory. The first really conclusive work was that of Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, **44**, 1866; 1923, **45**, 1106), who measured the hydrolytic adsorption of methylene-blue and of salts of various acid dyes by pure sugar charcoal activated at 1000° In 1924 Miller (*ibid.*, **46**, 1150) was able to show that after adsorption from sodium benzoate solution, the amount of acid in the charcoal was exactly equivalent to the amount of free alkali in the solution (with a 1200° charcoal). Kolthoff (*Rec. Trav. chim.*, 1927, **46**, 549; *Z. Elektrochem.*, 1927, **33**, 497), as a result of work on charcoals activated between 900° and 1000°, formulated a set of rules for hydrolytic adsorption of salts with reference to the capillary activity of the acids and bases from which the salts are formed. Various other workers have investigated the problem from different viewpoints, but almost without exception, the work has been carried out unsystematically and only on high-temperature charcoals.

Previous work in the present series has shown that the properties of charcoal vary very greatly with temperature of activation, the fundamental difference between high- and low-temperature charcoals being brought out very clearly by the results for the adsorption of acids and bases (Part IX, J., 1937, 1489). It was found that a 900° charcoal possessed maximum acid- and minimum base-adsorbing properties, the reverse being true of a 400° charcoal. At intermediate temperatures there was a gradual change from one type of charcoal to the other. These results suggested the subject of the present research. It seemed improbable that hydrolytic adsorption should be exclusively a property of high temperature charcoals, and likely that low-temperature charcoals would exhibit hydrolytic adsorption in the opposite direction to that of high-temperature charcoals, while at some intermediate temperature the hydrolytic adsorption would be zero. This has proved to be the case.

In view of the fact that, in general, organic acids and bases are very much more strongly adsorbed than inorganic acids and bases, it was decided to study the following three typical cases : (1) a salt of an inorganic base and an organic acid (sodium benzoate) ; (2) a salt of an organic base and an inorganic acid (methylene-blue) ; and (3) a salt of an inorganic acid and an inorganic base (potassium chloride). Both hydrolytic adsorption and molecular adsorption were measured with ten charcoals activated at temperatures ranging from 320° to 1100°. The results are given in the table. Results for molecular adsorption are expressed in all cases as amount of substance in equiv. × 10^{-5} adsorbed per g. of charcoal, and for hydrolytic adsorption as amount of acid or base in equiv. × 10^{-5} liberated per g. of charcoal. A negative sign indicates acid liberation, and a positive sign base liberation. The last two sets of results are for charcoals activated at the first of the two temperatures named and reactivated at the second. The adsorption of iodine from N/50-solution was also measured in order to obtain an estimate of the surface areas of each charcoal. By dividing all the values of hydrolytic and molecular adsorption by the corresponding iodine values, values were obtained which were taken as a measure of the adsorption per unit area. These values are plotted against temperature of activation in Figs. 1, 2, and 3. The results are to a large extent independent of the extent of the surface (except possibly in cases where steric affects are present, as mentioned below) and depend only upon the nature of the charcoal surface. Consequently, they allow a comparison to be made between samples of charcoal activated at different temperatures.

Temp. of activation.	Adsorption of KCl.		Adsorption of sodium benzoate.		Adsorption of methylene-blue.		Adsorption of iodine.
	Hydrolytic.	Molecular.	Hydrolytic.	Molecular.	Hydrolytic.	Molecular.	
320°	− 1·21	(+ 1·7)	0	22·5	− 0·55	2·38	215
410	− 1·60	(0)	0	16·0	− 0·62	5·70	241
440	− 1·98	(0)	0	14·9	− 0·65	16·0	348
500	+ 0·12	(+ 0·1)	0	9·5	0	8·65	308
590	+ 0·83	(+ 0·5)	+ 0·82	3·5	+ 0·8	9·90	388
740	+ 1·64	(+ 0·4)	+ 2·88	10·0	+ 1·9	10·1	309
810	+ 3·45	(− 0·3)	+ 11·6	43·0	+ 1·1	117	974
880	+ 2·35	(+ 1·0)	+ 11·5	43·3	+ 1·1	76	911
980	+ 1·66	(0)	+ 4·12	42·7	+ 0·4	125	627
1100	+ 1·51	(− 0·1)	+ 6·57	34·0	+ 0·2	85	586
880, 410	− 4·94	(0)	0	42·7	− 26	121	726
410, 880	+ 3·43	(+ 0·2)	+ 11·6	45·2	+ 1·1	169	928

FIG. 1.

Adsorption of potassium chloride.

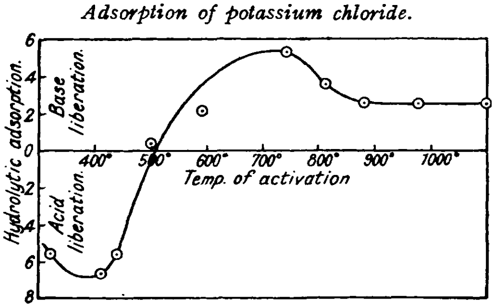
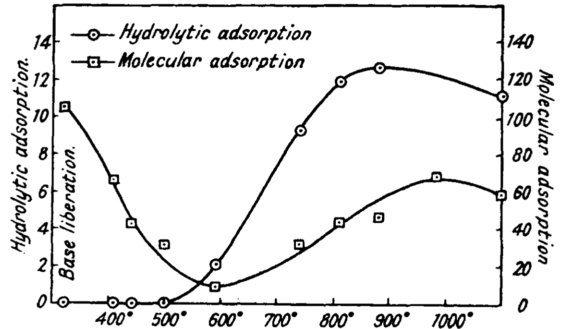


FIG. 2.

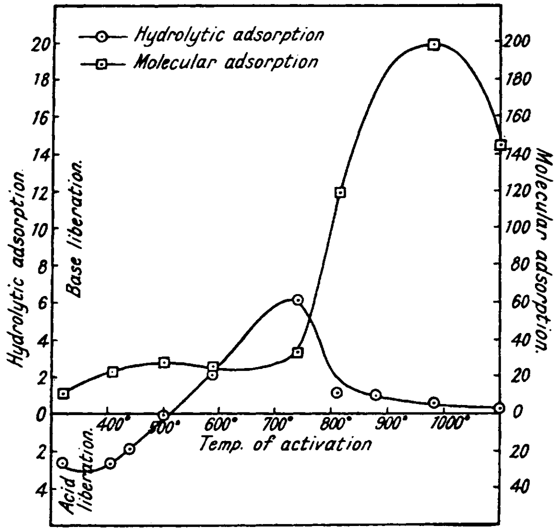
Adsorption of sodium benzoate.



The graphs show very clearly the difference between high- and low-temperature charcoals. Potassium choride and methylene-blue both show definite hydrolytic adsorption with maxima for charcoals activated at 350—400° (acid liberation), and 700—750° (base liberation). At present no explanation can be given of the fact that the second maximum for these two salts does not correspond with charcoals possessing maximum acid-adsorbing properties, *i.e.*, with charcoals activated at 850—900°. Presumably this shift of the maximum is connected in some way with the chloride ion, because in both cases the acid which is being adsorbed is hydrochloric acid (methylene-blue is the hydrochloride of a basic dye). Sodium benzoate gives a maximum at about 800°, and no hydrolytic adsorption below 500°. Below 500° very small amounts of acid were detected by titration, but the calculated results for adsorption per unit area were quite erratic. Although the amounts of charcoal used in the three cases varied considerably, the actual volumes of base used in the titrations were remarkably constant. The only other constant factor in the titrations was the volume of solution used, and it was suspected that the acid present was merely dissolved carbon dioxide, no attempt having been made to exclude this from the system. Calculation from the known solubility of carbon dioxide in water (at its partial pressure in the atmosphere) showed that this would account for the acidity actually measured. It was assumed, therefore, that no hydrolytic adsorption took place on charcoals activated below 500°. This is explained by the fact that comparatively large amounts of benzoic acid are adsorbed even by low-temperature charcoals (King, *loc. cit.*). Presumably both benzoic acid and sodium hydroxide are adsorbed at the same time, but the method of analysis used does not allow a distinction to be made between this type of adsorption and true molecular adsorption.

FIG. 3.

Adsorption of methylene-blue.



Sodium benzoate shows abnormally high values of molecular adsorption on low-temperature charcoals. Two factors contribute to this. In the first place, since the charcoal was prepared by heating sucrose to a comparatively high temperature, it will have acquired some of the properties of a high-temperature charcoal. At temperatures below about 400° the surface conditions characteristic of these temperatures are established quite slowly, and so the charcoal may retain some of the properties of high-temperature charcoals. If this happens, the amount of substance adsorbed may be greater than would be the case if the high-temperature surface had been completely destroyed. The second factor tending to increase the apparent molecular adsorption is the fact (see above) that below 500° benzoic acid and sodium hydroxide are adsorbed together.

The graph for methylene-blue shows a sudden sharp rise of molecular adsorption beyond 740° which may be attributed to steric effects (King, J., 1934, 1975). Above this point the ultra-pores, which are initially too small to admit the methylene-blue molecules, are sufficiently enlarged by oxidation to allow adsorption to take place. As would be expected from the size of the molecule, steric effects play a large part in the adsorption of methylene-blue. These effects are most striking in the case of hydrolytic adsorption below 500° where the large methylene-blue hydroxide molecules are being adsorbed. Activation at 880° followed by reactivation at 410° gave a 15-fold increase of hydrolytic adsorption. Molecular adsorption showed a 10-fold increase. This increase is due to the increase of available surface area by the enlarging of the ultra-pores at high temperature.

The results for the hydrolytic adsorption of methylene-blue by high-temperature charcoals do not agree with those of Bartell and Miller (*loc. cit.*), who found that charcoal activated at 1000° liberated acid from methylene-blue solutions. It should be pointed out, however, that the results are not strictly comparable because the experimental conditions were quite different. Bartell and Miller used 0·0025M-solutions with sufficient charcoal nearly to decolorise the solution, whereas in the present work 0·02N-solutions were used and the amount of charcoal was sufficient to remove only a small part of the dye from the solution.

In agreement with Miller and Kolthoff, it was found that potassium chloride is only hydrolytically adsorbed. Owing to difficulties of estimating potassium chloride in dilute solutions, the results for molecular adsorption (given in parentheses in the table) show sometimes a small positive and sometimes a small negative value. The assumption that molecular adsorption is zero is justified by the magnitude of the results and the inconsistency of the sign.

The graphs for molecular adsorption of the other two salts are interesting because they indicate that, even in cases where adsorption is not directly affected by the existence of specific surface oxides, temperature of activation may still have a considerable influence on the amount of adsorption. Very little work has been done on this influence, and it is not possible to say whether the type of curve obtained in the present work is of fundamental significance, or whether it is the result of a large number of factors, such as those mentioned above, all operating at the same time.

The general trend of the results for hydrolytic adsorption may be interpreted by the surface oxide theory, although it is evident that the surface of active charcoal and the mechanism of adsorption are far more complex than the theory suggests. The results for the two reactivations demonstrate the reversibility of surface conditions. In cases where steric effects are absent, the results for reactivated samples are very close to those for samples activated in the ordinary way at one temperature. In such cases the properties of the charcoal are characteristic of its activation temperature and independent of previous heat treatment. (These remarks refer, of course, to adsorption per unit area.) That hydrolytic adsorption is due to the presence of chemisorbed oxygen on the charcoal is shown by the fact that a sample of unactivated charcoal gave no appreciable hydrolytic adsorption. Kolthoff also noted this fact. Again, Burstein and Frumkin (*Z. physikal. Chem.*, 1929, **141**, 219) found that a sample of activated charcoal, out-gassed at 1000° and placed in a salt solution in a vacuum, gave no hydrolytic adsorption. After exposure to oxygen, however, hydrolytic adsorption reappeared. The general change of hydrolytic adsorption with temperature of activation is as would be expected from the surface oxide theory, but there is one significant fact that the theory does not explain. The curves show that all three salts used gave no hydrolytic adsorption with a charcoal activated at 500°. A consideration of the relative adsorbability of benzoic acid, hydrochloric acid, and strong bases shows that the position of zero hydrolytic adsorption, *i.e.*, the position where acid and base are equally adsorbed, should be different for different salts. No explanation of the observed facts can be suggested.

EXPERIMENTAL.

The charcoal used was prepared from " AnalaR " sucrose by charring it in a silica tube and heating it until no further fumes were evolved. After rough grinding, the charcoal was heated for 3 hours in a slow stream of carbon dioxide. No further attempt was made to purify the charcoal because such a purification involves treatment with hydrofluoric and hydrochloric acids, the last traces of which are extremely difficult to remove. The finely powdered charcoal was activated by 18 hours' heating in a silica tube furnace in a slow stream of moist oxygen (about 2 c.c. per minute). The temperature was measured by means of a thermocouple. After activation, the charcoal was removed from the furnace, tipped into a stoppered bottle, and quickly cooled.

The acid and base liberated during adsorption were estimated by electrometric titration with N/100-sodium hydroxide or hydrochloric acid, a glass electrode and a " Cambridge " valve electrometer being used. The titration vessel and electrodes were electrically shielded, and precautions against leakage currents were taken.

The total change in composition of the solutions was measured in order to obtain the molecular adsorption. Methylene-blue was estimated by titration with titanous sulphate, and chloride was estimated by Drechsel's modification of Volhard's method (*Z. anal. Chem.*, 1877, **16**, 351). A method for the estimation of benzoate similar to that of Henville (*Analyst*, 1927, **52**, 149) was used, except that the end-point was determined electrometrically with the glass electrode.

The following standard procedure was adopted for measuring the adsorption. 1—3 G. of charcoal were weighed into dry 6-oz. glass-stoppered bottles, and 150 c.c. of N/50-solutions of the various salts were run in. The bottles were vigorously shaken for a few minutes, and then left for 20 hours with occasional shaking. During the first stages of the adsorption, varying amounts of gas were evolved from the charcoal, especially from high-temperature samples. The solutions were filtered off through 7·0-cm. filter papers, and the first 10—15 c.c. of filtrate neglected; 100-c.c. portions of the filtrates were titrated with acid or alkali, and 25-c.c. portions were analysed to find the total adsorption. In general, the amount of acid or base in 100 c.c. of solution was equivalent to 0·5—8 c.c. of N/100-alkali or -acid. All the glass vessels were thoroughly steamed out before use. The solutions were kept as N/5-stock solutions, and diluted to the required strength immediately before use.

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