307. *Studies in Chemisorption on Charcoal. Part IX. The Influence of Temperature of Activation on the Sorption of Acids and Bases.*

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In previous papers of this series, the fundamental effects of temperature of activation on the properties of charcoal as an adsorbent and catalyst have been reported, and the results ascribed to the formation of specific surface oxides. Previous workers have noticed that charcoals activated at high temperatures have no power of adsorbing bases but are good acid adsorbents, while activations in the neighbourhood of 400° produce samples which adsorb bases. The adsorption of a number of acids and bases on pure charcoals activated at 15 different temperatures has now been measured, and an estimate made in each case of the adsorption per unit area. It appears that the adsorption per unit area of acids increases with temperature of activation up to about 850°, while over the same temperature range base adsorption falls to zero from a considerable value. Above 850°, base adsorption reappears to a slight extent, while that of acids decreases somewhat. These variations are in agreement with the changes in other properties with temperature of activation, already studied by the author.

In earlier parts of this series (J., 1935, 889; 1936, 1688; *Trans. Faraday Soc.*, 1934, **30**, 1094) the effect of the temperature of activation of charcoal in an atmosphere of oxygen on its adsorbent and catalytic properties has been discussed, and the fundamental variations ascribed to the existence of different surface oxides of carbon characteristic of the temperature of activation. The surface of charcoals which have been oxidised in the neighbourhood of 400° is acidic, and capable of adsorbing bases, while that produced at 850° is basic and will not remove alkalis from solution. The fundamental effect of temperature of activation on the properties of charcoal eluded the earlier investigators, but the exclusion of bases by high-temperature samples, and their adsorption by charcoals activated at relatively low temperatures, was observed by a number of workers (Kruyt and de Kadt, *Kolloid-Z.*, 1929, **47**, 44; Schilow, Shatunowskaja, and Tschmutow, *Z. physikal Chem.*, 1930, **149**, 211; Kolthoff, *J. Amer. Chem. Soc.*, 1932, **54**, 4473). Although these results are, collectively, fairly comprehensive and their implication clear, it was thought useful to measure the adsorption of a number of acids and bases on a pure charcoal surface activated at a larger number of temperatures, allowance being made for the increased activity due to surface extension by the more vigorous oxidation at the higher temperatures. It should thus become possible to relate variations of acid–base adsorption with temperature of activation to those of other properties of the pure charcoal surface, described in earlier parts of this series.

Measurement has therefore been made of the adsorption of hydrochloric, acetic, and benzoic acids, of sodium and ammonium hydroxides, and of iodine on pure sugar charcoals activated by heating in moist oxygen at different temperatures. It should be noticed that the molecules chosen for adsorption were all of small dimensions, so complications due to the steric effect of ultraporosity, first observed by Landt and Bhargava (*Z. Ver. deut. Zuckerind.*, 1929, **79**, 470) and discussed also by the present author (J., 1934, 1975), would be eliminated.

The results are expressed in the table as amount of adsorption in equivalents × 10^{-5} per g. of adsorbent. In the case of hydrochloric acid a few determinations were made of the amount of chloride adsorbed, as well as those in which the difference of hydrogen-ion concentration of the solution before and after adsorption was measured. In all these cases the adsorption of the chloride ion was the same as that of the hydrogen ion, in agreement with Kolthoff (*Rec. trav. chim.*, 1927, **46**, 594), who showed that the anions and cations of inorganic acids were adsorbed to an equal extent on pure charcoal.

It is immediately obvious from the table that the adsorption of both acids and bases is fundamentally influenced by the type of surface oxide, for the samples activated in the neighbourhood of 400° show a maximum base and minimum acid adsorption, whereas maximum acid and zero base adsorption corresponds to activation at *ca.* 850°.

Adsorption of acids and bases on pure charcoal.
(equivs. × 10^{-5} per g.).

No.	Temp.	I_2.	HCl.			$CH_3\cdot CO_2H$.		$C_6H_5\cdot CO_2H$.		NaOH.		NH_4OH.	
1	350°	75	2·8	2·75*	*0·37*	16·2	*2·16*	50·3	*6·7*	30·2	*4·03*	56·7	*7·54*
2	380	99	0	0	*0*	18·5	*1·87*	47·5	*4·8*	153	*15·5*	180	*18·2*
3	415	166	0	0	*0*	28·2	*1·70*	69·5	*4·18*	158	*9·51*	198	*11·9*
4	420	220	0	0	*0*	36·2	*1·66*	91·0	*4·14*	175	*7·96*	199	*9·05*
5	480	221	1·9	—	*0·08*	40·2	*1·82*	94	*4·25*	105	*4·76*	139	*6·25*
6	550	247	5·9	5·9	*0·24*	71·5	*2·89*	109	*4·43*	41	*1·66*	53	*2·14*
7	650	288	13·6	—	*0·47*	90·0	*3·12*	142	*4·87*	18	*0·62*	34	*1·18*
8	700	299	15·8	—	*0·53*	96·5	*3·23*	161	*5·38*	13·3	*0·44*	25	*0·84*
9	760	551	31·5	—	*0·57*	205	*3·71*	336	*6·10*	2·0	*0·36*	31·5	*0·57*
10	810	652	43·0	—	*0·66*	265	*4·05*	482	*7·39*	0	*0*	4·5	*0·07*
11	890	571	44·6	44·5	*0·78*	228	*3·98*	426	*7·44*	10·1	*0·18*	22·7	*0·39*
12	980	436	31·5	—	*0·72*	172	*3·95*	324	*7·42*	8·2	*0·19*	18·4	*0·42*
13	1030	493	33·0	—	*0·67*	185	*3·77*	274	*5·54*	13·8	*0·28*	35·0	*0·71*
14	890—420	715	31·2	—	*0·43*	113	*1·58*	288	*4·03*	232	*3·24*	33·8	*4·72*
15	420—830	784	67·0	—	*0·85*	317	*4·04*	599	*7·59*	0	*0*	2·4	*0·03*

* Values in this column represent the Cl^- ion.

As the temperature of activation is increased, oxidation becomes more vigorous and the surface area increases. This is indicated by the magnitude of the iodine adsorption, which increases from 75 to 784 according to the temperature and duration of the activation. Below 810°, the iodine adsorption increases steadily with temperature of activation; above 810° the results are not strictly comparable, as the time of activation was shorter than at the lower temperatures. In order to obtain a quantitative comparison of the areas of different samples of charcoal, a measurer must be employed, the adsorption of which is not influenced by changes in the chemical nature of the surface. For this purpose we have found iodine consistently satisfactory, and accordingly, we take the iodine adsorption values recorded in the table as proportional to the areas of the charcoals concerned.

The relative magnitudes of adsorption of acids and bases *per unit area of surface* are expressed by the numbers in *italics* in the table, where the measured adsorption per g. of charcoal has been divided by the iodine adsorption (equivs. $\times 10^{-4}$ per g.) of the same sample. The adsorption of acids is at a minimum (with zero or even negative adsorption in the case of hydrochloric acid) at 400°, and rises steadily to a maximum somewhere in the neighbourhood of 850°, after which it decreases somewhat; with bases, the adsorption is maximum at 400° and slowly decreases (to zero in the case of sodium hydroxide) until 850° is reached, after which it increases (adsorption reappears) again to a small extent. That these results are due to the constitution of the oxide surface produced at the temperature employed for activation, and not merely to the presence of tenaciously held impurities which are progressively removed on increasing the temperature, is shown by activations nos. 14 and 15. In the former, a charcoal activated at 890° (11), possessing considerable adsorptive power for acids and practically none for bases, becomes, after reheating in oxygen at 420°, only half as efficient as an acid adsorbent, while its base adsorption has increased to more than 10 times its former value. No. 15, a base-adsorbing 420° charcoal (4), after reactivation at 830°, would not remove any base from solution, and at the same time became much more efficient as an acid adsorbent.

The 350° activation produced a charcoal with greater acid and less base adsorption capacity than those prepared at slightly higher temperatures. This is probably due to the fact that, at this relatively low temperature, the charcoal surface which had been prepared by carbonising in air at about 700° still retained some of the oxide film characteristic of the higher temperature, and was thus not able to manifest to the full the acidic properties of the low-temperature activated surface.

The results of activations at very high temperatures are interesting, as the adsorption of bases increases (or reappears) while that of acids decreases above 850°. Although this is not in agreement with the observations of all previous workers (Miller prepares base-excluding charcoals at 1000°, and Dubinin reports but does not comment on a slight adsorption of sodium hydroxide on samples activated at that temperature), yet it agrees with earlier work in this series in which the p_H of charcoal suspensions in conductivity water fell considerably from a maximum for the 850° activation (J., 1935, 889) at which catalytic properties (J., 1936, 1688) also go through a point of inflexion. We are not yet in a position to discuss the nature of the change undergone by the carbon surface at 850°, but its effect on the properties of charcoal seems to be fundamental.

EXPERIMENTAL.

Pure sugar charcoal was prepared by carbonising AnalaR sucrose in a silica test-tube, followed by grinding and subsequent evacuation of the product at 750° in silica. The charcoal was then ground in an agate mortar, and screened to 100—200 mesh. As the ash content of the product was only 0·02%, it was considered unwise to subject it to any further purification, which would have involved treatment with acid.

The charcoal was activated by heating small samples, contained in silica trays, in a silica tube furnace in the presence of moist oxygen, as previously described (King and Lawson, *Kolloid-Z.*, 1934, **69**, 27), the treatment occupying 18 hrs. in activations 1—10 and a shorter period (8—15 hrs.) at the higher temperatures. The rate of flow of oxygen, which was reasonably uniform after the first few minutes, was about 5 c.c. per min. After as rapid cooling as possible, the charcoal was well mixed, and samples of approximately 0·5 g. added to a measured volume of the adsorbate solution. After standing for a day, with shaking, the solutions were filtered, first runnings rejected, and a measured proportion determined volumetrically.

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