932. *Fixation of Bromine from Aqueous Solution by Outgassed Charcoals.*

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Interaction of charcoal and aqueous bromine involves conversion of the halogen into hydrobromic acid as well as fixation by the charcoal. The amount converted depends on the acidity of the charcoal surface which varies with the amount of carbon dioxide complex present. The amount of fixation depends on the amount of the complex eliminated from the charcoal: one molecule of bromine is fixed for every two molecules of complex eliminated. Elimination of carbon monoxide complex does not increase the amount of bromine fixed. The degree of unsaturation in an outgassed charcoal seems to be a definite quantity. Bromine is fixed so firmly that only a small amount is desorbed as hydrobromic acid when the treated charcoal is degassed at 1200°. Fixation of bromine decreases porosity, increases sorption of moisture at relative vapour pressures below 0·5, and raises the heat of immersion in water.

WHILE studying adsorption isotherms of bromine on charcoal, Kolthoff[1] found that the halogen in aqueous solution changed rapidly into hydrobromic acid on coming into contact with the charcoal. Puri *et al.*[2] have shown that this conversion takes place only if the charcoal has not previously been outgassed at $\not<$750°, and that if it has been outgassed the reaction involves " fixation " of a certain amount of bromine. The present paper describes the effect of outgassing two varieties of charcoal, at gradually increasing temperatures, on the fixation of bromine in relation to the elimination of oxygen complexes, and the effect of this fixation on the porosity, the water isotherm, and the heat of immersion of the charcoal.

EXPERIMENTAL

Materials.—Charcoals were prepared by carbonisation of (1) recrystallised cane sugar and (2) cotton stalks. Sugar was carbonised by addition of pure sulphuric acid, followed by exhaustive washing with hot distilled water, and cotton stalks by burning small pieces in a limited supply of air at 350° in a Pyrex glass vessel surrounded by a heat-lagged nichrome coil for uniform electrical heating (current controlled with a Variac transformer). The charcoals were transferred to wide trays and allowed to cool in air. Sugar charcoal was almost free from ash; the other sample was extracted with hydrofluoric acid to lower the ash content to 0·17%. Portions (10-g.; oven-dried at 120°) of these charcoals (referred to below as " original " charcoals) were evacuated in a resistance tube-furnace at 300°, 400°, 500°, 700°, 900°, 1000°, and 1200°. The temperature was allowed to rise gradually and before it was raised another 50° complete elimination of the gases at the preceding temperature was ensured. After degassing at each temperature, the sample was allowed to remain and cool *in vacuo* and was then transferred to a stoppered bottle.

The amount of oxygen retained, and its nature, in each sample were estimated by evacuating 2-g. portions at 1200° by gradually raising the temperature as described above, collecting water in calcium chloride tubes, carbon dioxide in a series of Erlenmeyer flasks containing a known amount of barium hydroxide solution, and carbon monoxide in cuprous chloride solution in an Orsat–Lunge gas-analysis apparatus in the usual way. The amount of total oxygen evolved as water, carbon dioxide, and carbon monoxide was in close agreement with the oxygen obtained by ultimate analysis of the charcoal (Table 1).

Since elementary hydrogen in carbons is not eliminated completely even on degassing at 1200°,[3] this value was determined by ultimate analysis with due correction, where necessary, for the amount of water contained in the sample.

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[1] Kolthoff, *Rec. Trav. chim.*, 1929, **48**, 291.

[2] Puri, Mahajan, and Singh, *J. Indian Chem. Soc.*, 1961, **38**, 943.

[3] Anderson and Emmett, *J. Phys. Chem.*, 1952, **56**, 753; Emmett, *Chem. Rev.*, 1948, **43**, 69; Puri, Myer, and Sharma, *Chem. and Ind.*, 1956, 30.

It is seen (Table 1) that the original charcoals contain appreciable amounts of oxygen that are evolved as carbon dioxide and carbon monoxide; hydrogen is evolved as steam up to 700°, and above that as hydrogen. The amount of oxygen evolved as carbon dioxide decreases with rise in temperature much more rapidly than that evolved as carbon monoxide. Thus the amount of carbon dioxide complex decreases much more than that of the carbon monoxide complex on degassing at 300°, 400°, and 500°; the former is absent after degassing at 500—700°, while the second complex becomes absent only between 1000° and 1200°. Hydrogen continues to be evolved even up to 1200°.

TABLE 1.

Oxygen and hydrogen complexes and pH values of aqueous suspensions of the various samples of charcoal.

Treatment		O_2 (mg./g.) evolved as			Total O_2 evolved (mg./g.)	Total O_2 by analysis (mg./g.)	H_2 (mg./g.)	pH in H_2O
		CO_2	CO	H_2O				
				Sugar charcoal				
Original		116	89	91	296	288	34	3·0
Outgassed at:	300°	62	86	87	235	234	33	3·4
	400	33	84	79	196	191	34	3·9
	500	10	69	50	129	126	31	4·8
	700	0	61	45	106	103	26	6·9
	900	0	21	0	21	19	17	7·7
	1000	0	7	0	7	8	11	8·4
	1200	0	0	0	0	0·04	10	8·6
				Cotton stalk charcoal				
Original		54	64	69	187	184	31	3·6
Outgassed at:	300°	36	64	68	168	172	31	4·3
	400	20	63	62	145	140	30	4·9
	500	9	63	60	132	126	30	5·5
	700	0	49	43	92	93	25	6·9
	900	0	14	0	14	13	16	7·5
	1000	0	6	0	6	7	10	8·4
	1200	0	0	0	0	0	9	8·5

pH values of the various samples were determined by means of a glass electrode, after shaking of their aqueous suspensions (2·5%) in freshly distilled, carbon dioxide-free, water for 6 hr. The values are included in Table 1.

An aqueous solution ($\sim$0·1N) of bromine in potassium bromide (2 moles per mole of bromine) was used for the reaction.

Procedure.—The effect of temperature and time of contact was studied first by keeping 1-g. portions of the original sugar charcoal and of those degassed at 700° and 1200°, mixed with 200 ml. of the bromine solution, in incubators thermostatically controlled at 22° and 32°, for different times. There was a slight difference in the amount of reaction at the two temperatures in the initial stages, but ultimately towards the approach of the end-point, after 60—65 hr., the two values became almost identical. Subsequently the temperature of one of the incubators was raised to 35° but there was hardly any change in the final values. As the temperature variation had little or no effect on the ultimate results, it was considered more convenient to shake the suspensions mechanically, the end-point being approached within 24 hr. The following procedure was, therefore, adopted.

Charcoal (1 g.) was shaken mechanically with bromine solution (200 ml.) in 500-ml. stoppered bottles, wrapped in thick black paper, for 24 hr. (necessary for the attainment of the end-point), after which the suspension was filtered and the charcoal repeatedly washed with distilled water. The filtrate and washings were made up to a known volume and an aliquot part was analysed for free bromine by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate solution [4] and then for hydrobromic acid by titration against sodium hydroxide.

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[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., New York, 1948, p. 191.

A blank was also run every time; there was no noticeable change in the composition of the solution in the absence of charcoal. None of the charcoals liberated hydrobromic acid from the solution of potassium bromide in the absence of bromine.

Density and Porosity.—Density measurements (true, D_t, and bulk, D_b) were made by using benzene and mercury as displacement liquids.[5] Pore space (V_p) per 100 g. of charcoal was obtained from the equation, $V_p = 100(1/D_b - 1/D_t)$.

Water Isotherms.—Water-adsorption isotherms were determined [6] at 25°.

Heat of Immersion.—Samples (3—4 g.; oven-dried at 120°) were measured into thin-walled glass bulbs and outgassed for 10 hr. The calorimeter and technique were essentially as described by Boyd and Harkins.[7]

RESULTS AND DISCUSSION

Table 2 shows that in presence of the original charcoals an appreciable amount of bromine is converted into hydrobromic acid, but that only a small amount of it is " fixed." In presence of the outgassed samples the amount of bromine converted into hydrobromic acid decreases while the amount " fixed " increases with increase in the temperature of outgassing. The formation of hydrobromic acid, the genesis of which has been explained previously,[2] is minimum, and the fixation of bromine maximum, in presence of the charcoals outgassed at 700°. There is little or no change in these values when the charcoals are degassed at 900°, 1000°, and 1200°.

TABLE 2.

Reaction of charcoal (1 g.) with 0·11075N-aqueous bromine (in KBr) (200 ml., 22·15 milliequiv.).

(All amounts are milliequiv.)

Treatment		Un-changed Br	HBr formed	Br fixed by charcoal		Un-changed Br	HBr formed	Br fixed by charcoal	
				by diff.	by anal.			by diff.	by anal.
		Sugar charcoal				*Cotton stalk charcoal*			
Original		7·77	13·93	0·45		12·30	9·32	0·53	
Outgassed at:	300°	8·39	11·71	2·05	1·98	12·82	8·26	1·07	
	400	11·00	8·03	3·12		14·10	6·55	1·50	1·56
	500	12·65	5·82	3·68	3·58	16·69	3·59	1·87	
	700	17·68	0·32	4·15		19·55	0·30	2·30	2·39
	900	17·73	0·32	4·10	4·21	19·62	0·25	2·28	
	1000	17·60	0·35	4·20		19·60	0·30	2·25	2·17
	1200	17·67	0·33	4·15	4·06	19·58	0·27	2·30	

Comparison with Table 1 shows that the capacity of charcoal to convert bromine into hydrobromic acid depends upon its acidity and varies as the amount of carbon dioxide complex (*i.e.*, the oxygen complex capable of evolving carbon dioxide) contained in it. When this complex is completely eliminated at 700° and the charcoal surface is no longer acidic, there is little or no formation of hydrobromic acid.

The fixation of bromine increases with elimination of carbon dioxide complex. It appears that bromine is added at the sites rendered vacant by decomposition of this complex.

The relation between the amount of carbon dioxide eliminated and the amount of additional bromine fixed is shown in Table 3. Nearly one mole of bromine is fixed for the elimination of 2 moles of this complex. This is so for both charcoals and for each temperature of outgassing. It appears that each molecule of this complex involves a single

[5] McDermot and Arnell, *J. Phys. Chem.*, 1954, **58**, 492.

[6] Puri, Lakhanpal, and Verma, *J. Indian Chem. Soc.*, 1952, **29**, 841.

[7] Boyd and Harkins, *J. Amer. Chem. Soc.*, 1942, **64**, 1190.

TABLE 3.

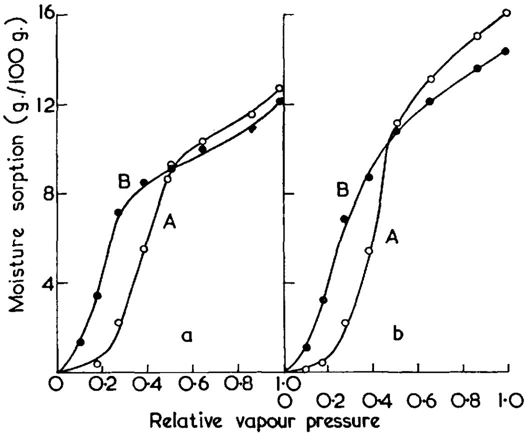
Bromine fixed by charcoal in relation to the carbon dioxide complex eliminated and bromine desorbed on outgassing the treated material at 1200°.

(All quantities are mmole/g.)

Treatment		Br fixed by charcoal	Further Br fixed on degassing	Decrease in CO_2 complex on degassing	Br as HBr on degassing at 1200°	Br fixed by charcoal	Further Br fixed on degassing	Decrease in CO_2 complex on degassing
			Sugar charcoal			*Cotton stalk charcoal*		
Original		0·225	—	—	—	0·265	—	—
Outgassed at:	300°	1·025	0·80	1·69	0·35	0·535	0·27	0·56
	400	1·56	1·335	2·59	0·675	0·75	0·485	1·06
	500	1·84	1·615	3·31	0·735	0·935	0·67	1·41
	700	2·075	1·85	3·625	0·875	1·15	0·885	1·69
	900	2·05	1·825	3·625	—	1·14	0·875	1·69
	1000	2·10	1·875	3·625	—	1·125	0·86	1·69
	1200	2·075	1·85	3·625	0·385	1·15	0·885	1·69

carbon atom of the charcoal, two molecules of the complex being adjacent, so that when two molecules of the complex are eliminated a double-bond site is created between the two adjacent carbon atoms.

It is also evident that the elimination of oxygen evolved as carbon monoxide does not create additional unsaturated sites because, although outgassing at temperatures above 700° results in progressive elimination of this form of oxygen (Table 1), there is no further increase in the amount of bromine fixed.



Water isotherms for sugar charcoal outgassed at (a) 700° and (b) 1200°, (A) before and (B) after treatment with bromine.

These observations should be useful in the study of surface chemistry of charcoal and in understanding the nature and structure of surface oxygen complexes about which opinions vary.[8]

It has been shown [9] that treating a degassed charcoal with a solution of a mild oxidising agent such as potassium persulphate results in fixation of some oxygen. It was thought of interest to study the combined effect of oxidation and bromination. For this purpose 2-g. portions of charcoal degassed at 1200° were first treated with potassium persulphate solutions of various concentrations and then with 0·1N-bromine solution in the usual way. The amounts of oxygen and bromine fixed were determined by ultimate analysis. The

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[8] Kipling, *Quart. Rev.*, 1956, **10**, 1; Garten and Weiss, *Rev. Pure Appl. Chem.* (*Australia*), 1957, **7**, 69; Smith, *Quart. Rev.*, 1959, **13**, 282.

[9] Puri, Mahajan, and Singh, *J. Indian Chem. Soc.*, 1961, **38**, 135.

results (Table 4) show that the total of both oxygen and bromine remains almost the same for a given charcoal. It appears, therefore, that oxygen and bromine are fixed at the same unsaturated sites and that the amount of unsaturation in a charcoal is a definite quantity.

In order to see if bromine fixed by charcoal can be recovered on high-temperature evacuation some of the outgassed samples treated with bromine solution were placed in a vacuum at 1200°. Bromine as such was not detected in the gaseous products. However, a small amount was evolved as hydrobromic acid, presumably by combination (at the prevailing high temperature) with the hydrogen contained in the charcoal or by interaction with traces of moisture which may have been picked up by the material during transference, etc. The values are included in Table 3. An appreciable amount of bromine is still retained by the charcoal even after this drastic treatment.

TABLE 4.

Fixation of oxygen and bromine on charcoal outgassed at 1200°.

(Quantities are mmole/g.)

O_2 chemisorbed	Br fixed	O_2 chemisorbed + Br fixed	O_2 chemisorbed	Br fixed	O_2 chemisorbed + Br fixed
	Sugar charcoal			*Cotton stalk charcoal*	
0·00	2·07	2·07	0·00	1·15	1·15
0·53	1·34	1·87	0·42	0·59	1·01
0·79	1·06	1·85	0·87	0·19	1·06
1·04	0·89	1·93			
1·32	0·58	1·90			

TABLE 5.

Effect of " bromination " on porosity and heat of wetting of sugar charcoal.

	Pore space (c.c./100 g.)		Heat of wetting (cal./g.)	
Treatment	before	after	before	after
Outgassed at: 700°	90·9	70·1	3·87	7·75
1200	90·5	68·5	3·68	7·37

The fixation of bromine causes an appreciable decrease in the porosity of the charcoal (Table 5). The water isotherms (Figure) also undergo a noticeable change. The treated samples pick up considerably more moisture up to 50% relative humidity and slightly less thereafter, the curves for the treated and the untreated samples intersecting at about 50% relative humidity. These observations indicate that a considerable narrowing of the capillary pores takes place as a result of fixation of bromine. The enhanced water sorption at lower humidities appears to be due partly to narrowing of capillary pores and partly to decrease in hydrophobic (or increase in hydrophilic) character, which is also indicated by an appreciable increase in the heat of wetting of charcoal in water after fixation of bromine (Table 5).

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