INTERACTION OF OZONISED OXYGEN WITH MICROCRYSTALLINE CARBONS

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Interactions of charcoals, carbon blacks and activated carbons with ozone, mixed in oxygen upto 2.5 per cent, in aqueous and nonaqueous media as well as in dry state at ambient temperature, have been investigated amongst others by Deitz and Bitner (1,2), Donnet and coworkers (3,4,5) and Puri et al (6). The reactions involve, amongst other things, gasification of the carbon, chemisorption of oxygen and formation of degradation products if water is used as the medium (4,5,6). The intensity of interaction is less if a nonaqueous liquid is used as the medium. Suitable mechanisms have been proposed (1,2,4,5). Nitrogen adsorption (77.4°K) on charcoal after the interaction showed a significant fall (2). The data on carbon blacks indicated development of microporosity in the products (3). The present paper relates to the study of the nature of the surface oxygen complexes formed and alterations in surface unsaturation and surface area produced on the interaction of a few microcrystalline carbons with ozonised oxygen (~2.5 per cent ozone) at 30°C.

Materials and Methods

Two samples of ash-free charcoal, prepared by the carbonisation of cane sugar and coconut shells and outgassed at 750° and 1000°C(7), nine samples of carbon blacks and a sample of commercial steam-activated carbon were used. Carbon (5g) was taken in a porcelain tube (dia = 5-in or 12.5 cm) which was kept in a thermostat (30°C±0.1°) and connected on one side to an ozoniser (Gallenkamp,GE-150) and to a series of conical flasks, containing known volumes of standard (0.2N) baryta solution (for estimating carbon dioxide formed), on the other . Ozonised oxygen (~2.5 per cent ozone) was passed at the rate of 2l/hr over the carbon bed, kept rotating at 18-20 revolutions per min, for 24 hr. The carbon was then withdrawn, stored under nitrogen and examined for (i) oxygen content by evacuating 1g material at 1000°C and analysing the gases (CO_2,CO and H_2O) evolved (8); (ii) barium hydroxide values as a measure of surface acidity(9); (iii) bromine value as a measure of surface unsaturation (7); and (iv) surface area by determining adsorption isotherms of carbon dioxide at 0°C and applying Dubinin equation(10).

Results and Discussion

The amount of carbon 'burnt' as carbon dioxide during the reaction extended for 24 hr and that of oxygen chemisorbed and recovered as CO_2,CO & H_2O on high temperature-evacuation are given in Table I. The gasification is seen to be maximum in the case of activated carbon and to be comparatively more in charcoals than in carbon blacks. It is significant to note that nearly 7 per cent of oxygen by weight could be added to each charcoal as well as to the activated carbon on treatment in ozonised oxygen at 30°C. The amount added to carbon blacks, however, is less and varies from 2 to 3 per cent by weight. The chemisorbed oxygen is seen to give rise to both CO- and CO_2-surface complexes. In the case of carbon blacks the interaction also involves partial conversion of CO- into CO_2-surface complex. The elimination of a part of the oxygen as water vapour appears to be due to fixation of oxygen at sites containing residual hydrogen in the carbons. The amount of carbon 'burnt' and that of oxygen chemisorbed in a given material is comparatively less than the value obtained when the interaction at the same temperature was studied in aqueous medium (6).

The CO_2-complex formed in each case was found to be partly acidic and partly nonacidic (11). The non-acidic (or neutral) complex is considered to arise from fixation of oxygen at certain unsaturated sites, measured by bromine value,and, therefore, to cause a corresponding fall in the bromine value (11). In the present case, however, the amount of the nonacidic complex formed is much more than the fall in bromine value observed. It appears probable that the treatment in ozone results in creating more unsaturated sites. This was checked by outgassing the charcoals at 750° so as to eliminate the entire CO_2-complex. The bromine values were redetermined and found to be appreciably higher (by over 35 % in most cases) than the initial values. The role of unsaturated sites in improving catalytic performance of carbons has been emphasised in previous publications (12).

The interaction is seen to cause a considerable rise in surface area,by about 50 per cent in carbon blacks and 90-100 per cent in 700°- and 1000°- sugar charcoals; the value for the activated carbon,however, shows a fall by about 40 per cent(cf.Table I). The interaction in the case of sugar charcoals was then continued for longer periods. The values showed a rise upto 48 hours treatment and then became 1178 and 1136 m^2g respectively. Beyond that there was a decline & the values decreased to 965 and 878 m^2/g after 80 hours of the

Table I

Effect of interaction of carbons with ozonised oxygen at 30°C on gasification of carbo chemisorption of oxygen & surface area of products.

Sample	Amount of carbon gasified (g/100g)		Oxygen content(g/100g)evolved as CO_2	CO	H_2O	Total	Surface area (m^2/g)
SC-750°C	3.05	(a)	nil	1.92	nil	1.92	550
		(b)	2.66	3.02	1.67	7.35	1040
SC-1000°C	3.92	(a)	nil	nil	nil	nil	323
		(b)	2.60	1.92	1.52	6.04	720
CC-750°C	2.20	(a)	nil	2.14	nil	2.14	562
		(b)	3.20	2.75	2.76	8.71	851
CC-1000°C	5.88	(a)	nil	nil	nil	nil	537
		(b)	2.86	1.68	2.33	6.87	885
Active Carbon	9.33	(a)	1.04	1.47	2.84	5.35	1005
		(b)	5.57	1.36	6.32	13.25	608
Philblack-A	1.21	(a)	0.19	0.33	0.13	0.65	46
		(b)	1.73	nil	2.11	3.84	76
Philblack-E	1.36	(a)	0.40	0.41	0.44	1.25	132
		(b)	1.80	0.30	2.17	4.27	182
Philblack-I	1.56	(a)	0.35	0.63	0.36	1.34	103
		(b)	1.73	0.30	2.63	4.66	160
Spheron-4	2.00	(a)	0.54	2.83	0.70	4.07	224
		(b)	3.36	1.45	2.51	7.32	291
Spheron-6	2.25	(a)	0.50	2.12	0.46	3.08	138
		(b)	2.07	1.30	2.39	5.76	229
Spheron-9	2.60	(a)	0.54	1.93	0.71	3.18	151
		(b)	2.75	1.16	2.68	6.59	221
Spheron-C	1.85	(a)	0.58	2.00	2.60	3.18	288
		(b)	3.95	1.57	2.71	8.23	361
Mogul	1.31	(a)	2.21	4.18	1.44	7.83	324
		(b)	3.95	2.86	3.71	10.52	410
Elf-O	1.43	(a)	1.18	2.17	0.71	4.06	209
		(b)	3.26	1.40	2.97	7.63	300

SC = Sugar charcoal; CC = Coconut shell charcoal; (a) = Before interaction; (b) = After interaction.

treatment. It appears that if oxidation in steam around 800° or in ozone at 30° enhances surface area by the creation of more kinks, corners, edges etc., these very structures get 'burnt' on continued exposure to oxidising atmosphere.

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