

Adsorption of Chlorine by Carbons from Solutions in Carbon Tetrachloride

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Adsorption of chlorine from solution in carbon tetrachloride by carbons, including charcoals, carbon blacks and activated carbons, at 30° is shown to be partly reversible and partly irreversible. The reversible adsorption appears to be due to surface effects while the irreversible adsorption is found to be due to chemisorption partly in substitution for hydrogen, partly by addition at the unsaturated sites and partly by fixation at some of the active sites constituted by edges, corners and discontinuities on the surface. The irreversibly held chlorine causes a considerable fall in the effective surface area particularly in the case of activated carbons. The carbon-chlorine complex is shown to have a high thermal stability. The data indicate that chlorine is chemisorbed at different sites of varying degrees of energies on placing carbons in contact with chlorine solution in carbon tetrachloride.

ADSORPTION of chlorine by carbons, including charcoals, carbon blacks and activated carbons, at ambient temperature from aqueous solutions has been reported by Puri et al.^{1,2} as well as by Rivin and Aron.³ The process involves hydrolysis of chlorine to hydrochloric acid and chemisorption of oxygen in the initial stages (1) and simultaneous chemisorption of both oxygen and chlorine in the later stages (2). Macrae and Oxtoby⁴ studied adsorption of chlorine by coals from non-aqueous solutions at 20° and 60° and found progressive removal of hydrogen from the coals, yielding hydrogen chloride, as well as appreciable chemisorption of chlorine by the coals. The perusal of the literature shows that the interaction of chlorine dissolved in a non-aqueous solvent with carbons other than coals has not been investigated. The use of a non-aqueous solvent avoids the complications caused by the formation of H⁺ and Cl⁻ ions as happens when water is used as the solvent. The effect of chemisorbed chlorine in altering effective surface areas of carbons has also not been looked into so far. The present work was, therefore, undertaken.

Experimental

Materials : Six carbon blacks, two ash-free charcoals prepared by the carbonisation of cane sugar and coconut shells (1) and three commercial activated carbons labelled as B, D and E were used. Their specific surface areas were calculated from adsorption isotherms of carbon dioxide determined at 273°K⁵ and surface unsaturation from the amount of bromine adsorbed irreversibly on treatment with aqueous bromine⁶. The hydrogen contents were determined by ultimate analysis. Chlorine was prepared by reacting hydrochloric acid (C.P.) with potassium dichromate (C.P.) and purified and dried by the usual methods. It was dissolved in carbon tetrachloride (A. R.) for the reaction.

Procedure : Two portions of carbon (1 g each) were mixed separately with 100 ml chlorine solution of a given concentration in stoppered pyrex-glass bottles wrapped in thick black papers. The suspensions were shaken for a few minutes to effect proper wetting and then allowed to stand with occasional shaking in an incubator maintained at (30°±0.1°) for a required interval of time. The fall in concentration of chlorine, in one case, was estimated by withdrawing an aliquot of the clear supernatant liquid, adding potassium iodide and a known excess of sodium thiosulphate and back titrating against standard iodine solution in the usual way. The amount of HCl formed, if any, was estimated by titrating the same solution against standard sodium hydroxide. To the second suspension as a whole, potassium iodide and a known excess of sodium thiosulphate were added and the mixture allowed to stand in the thermostat for 30 minutes which, in a number of preliminary experiments, was found sufficient to permit 'desorption' of the reversibly adsorbed chlorine. An aliquot was then back titrated against standard iodine. The fall in concentration of chlorine in the first case gave the total amount of chlorine adsorbed while that in the second case gave the amount of chlorine adsorbed irreversibly. The difference between the two gave the amount of chlorine adsorbed reversibly.

Results and Discussion

The total amount of chlorine adsorbed and that of HCl formed on interacting two of the carbons with chlorine solutions of different concentrations for 24 hours are plotted in Figure 1. It is seen that the extent of each reaction increases with rise in concentration of the solution and tends to approach a limiting value as the concentration approaches 0.3 N. The effect of time of contact, using 0.3 N

solution is also shown in the same figure. It appears that 10-12 hrs. contact is sufficient to get the final value in each reaction.

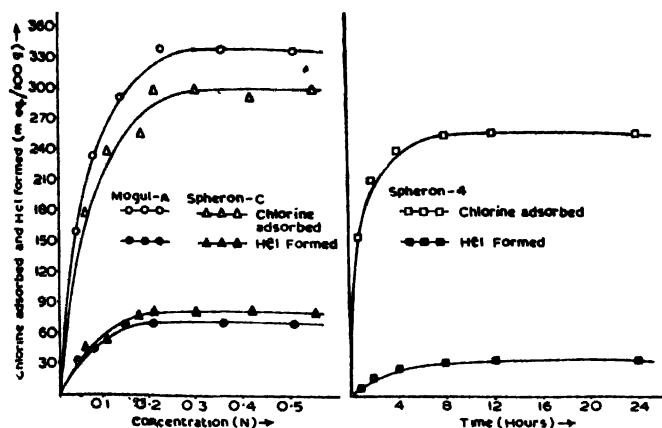
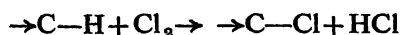


Fig. 1. Effect of concentration of Chlorine and the time of contact on the extent of Chlorine-Carbon reaction.

The formation of HCl in the present experiments cannot be due to hydrolytic adsorption of chlorine as has been observed in the case of interaction with aqueous chlorine¹. It appears highly probably that HCl is formed through substitution of chlorine for hydrogen, initially present in the carbons, by the reaction



as has been suggested in the case of similar substitution of bromine by previous workers⁷. This indicates possibility of fixation of an equivalent amount of chlorine in substitution for hydrogen in the various carbons.

The amounts of HCl formed and chlorine adsorbed reversibly as well as irreversibly, on keeping various carbons in contact with 0.3N solution for 24 hours are given in Table 1. The hydrogen contents, specific surface areas and surface unsaturations are also included in the table. It appears that only a small fraction of the hydrogen can be substituted by chlorine. In this connection it may be noted that Anderson and Emmett⁸ as well

as Puri and Bansal⁹ are of the view that only a small fraction of the combined hydrogen is present on the surface and that the rest of it is dispersed in more than one layer in the interior of the particles.

Physical adsorption of chlorine may be due to surface effects. However, the amount adsorbed could not be related to surface area as the carbons used differed widely in porosity and pore-size distributions. Chemisorption of chlorine is seen to be considerably higher than the HCl formed. It appears that the process involves not only simple substitution but also addition at the unsaturated sites. This view was supported by the observation that surface unsaturation which was appreciable initially (cf. column 4) fell to zero after the interaction. This indicates fixation of an equivalent amount of chlorine by the addition process.

In order to get some more insight, two of the carbon blacks as well as sugar and coconut charcoals were outgassed at 600° and 1000° before studying their interaction with chlorine solution in the same manner. The amounts of HCl formed and chlorine chemisorbed are given in Table 2. The values obtained earlier when these carbons had not been outgassed are also reproduced for easy comparison. It is observed that the amount of HCl formed increases as each carbon is outgassed at 600° and decreases as it is outgassed at 1000°. It appears that a part of the hydrogen held within the interior of the particles tends to diffuse out to the surface with increase in kinetic energy of the molecules as the carbons are heated to 600°. This enhances the interaction with chlorine yielding a larger amount of HCl. But when the carbons are evacuated at 1000° very little residual hydrogen is left¹⁰ for reacting with chlorine. The chemisorption of chlorine is seen to rise considerably as the carbons are outgassed. This appears to be due to increase in surface unsaturation (column 3) on elimination of surface oxygen complexes⁶.

Considering that a part of the chemisorbed chlorine, equivalent to HCl formed, is fixed in substitution for hydrogen and a part, taken as equivalent to initial surface unsaturation (which

TABLE 1—INTERACTION OF VARIOUS CARBONS WITH CHLORINE DISSOLVED IN CARBON TETRACHLORIDE AT 30°

| Sample | Surface area (m ² /g) | Hydrogen content (millieq/100 g) | Surface unsaturation (millieq/100 g) | Amount of HCl formed (millieq/100 g) | Amount of Chlorine (millieq/100 g) | |
|---------------------------|----------------------------------|----------------------------------|--------------------------------------|--------------------------------------|------------------------------------|-------------|
| | | | | | Adsorbed physically | Chemisorbed |
| Philblack-E | 132 | 310 | 13 | 20 | 55 | 60 |
| Spheron-4 | 224 | 478 | 45 | 36 | 81 | 177 |
| Spheron-6 | 138 (110) | 520 | 62 | 28 | 57 | 148 |
| Spheron-C | 288 (209) | 330 | 70 | 80 | 117 | 183 |
| Mogul-A | 252 (176) | 510 | nil | 72 | 217 | 123 |
| Mogul | 324 (186) | 480 | nil | 48 | 138 | 252 |
| Active Carbon B | 1005 (309) | 2620 | 155 | 37 | 106 | 680 |
| Active Carbon D | 801 (186) | 2360 | 139 | 63 | 220 | 620 |
| Active Carbon E | 550 (141) | 1940 | 125 | 52 | 74 | 373 |
| Original Sugar charcoal | 338 | 2940 | 86 | 200 | 104 | 376 |
| Original coconut charcoal | 372 | 2260 | 96 | 72 | 143 | 244 |

TABLE 2—EFFECT OF OUTGASSING CARBON BLACKS AND CHARCOALS ON ADSORPTION OF CHLORINE AND FORMATION OF HCl ON TREATMENT WITH CHLORINE DISSOLVED IN CARBON TETRACHLORIDE AT 30°

| Sample | Surface area (m ² /g) | Surface unsaturation (millieq/100 g) | Amount of HCl formed (millieq/100 g) | Amount of Chlorine chemisorbed (millieq/100 g) |
|-------------------------------|----------------------------------|--------------------------------------|--------------------------------------|--|
| <i>Spheron-C</i> | | | | |
| Original | 288 | 70 | 80 | 183 |
| Outgassed at 600° | — | 85 | 108 | 272 |
| Outgassed at 1000° | — | 88 | 26 | 149 |
| <i>Mogul-A</i> | | | | |
| Original | 252 | nil | 72 | 123 |
| Outgassed at 600° | 278 | 62 | 100 | 193 |
| Outgassed at 1000° | 182 | 70 | 23 | 164 |
| <i>Sugar Charcoal</i> | | | | |
| Original | 338 | 86 | 200 | 376 |
| Outgassed at 600° | 660 | 376 | 228 | 657 |
| Outgassed at 1000° | 323 | 405 | nil | 488 |
| <i>Coconut shell charcoal</i> | | | | |
| Original | 372 | 96 | 72 | 244 |
| Outgassed at 600° | 692 | 339 | 92 | 597 |
| Outgassed at 1000° | 423 | 352 | nil | 490 |

TABLE 3—ACCOUNT OF CHLORINE ADSORBED IRREVERSIBLY BY VARIOUS CARBONS

| Sample | Total chlorine irreversibly adsorbed (millieq/100 g) | Amount fixed possibly in substitution for hydrogen (millieq/100 g) | Amount fixed possibly by addition at unsaturated sites (millieq/100 g) | Amount of chlorine unaccounted for (millieq/100 g) |
|-------------------------|--|--|--|--|
| (1) | (2) | (3) | (4) | (5) |
| Philblack E | 60 | 20 | 13 | 27 |
| Spheron-4 | 177 | 36 | 45 | 96 |
| Spheron-6 | 148 | 28 | 62 | 58 |
| Mogul | 252 | 48 | nil | 204 |
| Active Carbon B | 680 | 37 | 155 | 488 |
| Active Carbon D | 620 | 63 | 139 | 418 |
| Active Carbon E | 373 | 52 | 125 | 196 |
| <i>Spheron-C</i> | | | | |
| Original | 183 | 80 | 70 | 33 |
| Outgassed at 600° | 272 | 108 | 85 | 79 |
| Outgassed at 1000° | 149 | 26 | 88 | 35 |
| <i>Mogul-A</i> | | | | |
| Original | 123 | 72 | nil | 51 |
| Outgassed at 600° | 193 | 100 | 62 | 31 |
| Outgassed at 1000° | 164 | 23 | 70 | 71 |
| <i>Sugar charcoal</i> | | | | |
| Original | 376 | 200 | 86 | 90 |
| Outgassed at 600° | 657 | 228 | 376 | 53 |
| Outgassed at 1000° | 488 | nil | 405 | 83 |
| <i>Coconut charcoal</i> | | | | |
| Original | 244 | 72 | 96 | 76 |
| Outgassed at 600° | 597 | 92 | 339 | 166 |
| Outgassed at 1000° | 490 | nil | 352 | 138 |

falls to zero after the reaction) is fixed by addition at the unsaturated sites. It is observed from the data presented in Table 3 that an appreciable amount of chemisorbed chlorine remains 'unaccounted for' in each case. It appears quite likely that some chlorine is also chemisorbed at certain other active sites, constituted, probably by edges, corners and discontinuities or is entrapped within some of the pores of the adsorbents and requires energy of activation to diffuse out of the system.

The specific surface areas of some of the carbons after chemisorption of chlorine were also determined. These are given in parentheses in Table 1. There is, evidently, an appreciable fall in surface area in each case, particularly so in the case of active carbons which are known to be highly porous. It appears that chemisorbed chlorine occupies a considerable proportion of the internal surface in carbons.

Thermal stability of carbon-chlorine surface

complex resulting from chemisorption of chlorine was checked by determining the amount of chlorine eliminated on outgassing some of the chlorinated carbons at gradually increasing temperatures. It was found that chlorine could be recovered only as HCl, presumably due to combination with the residual hydrogen held by the carbons. The elimination as HCl was found to commence only at 400° (Fig.2) in the case of Spheron-C, which is known to be essentially non-porous, and to stop at 600° even though only 30 milliequivalents out of the total of 272 milliequivalents of chlorine could be thus recovered. The residual chlorine could not come off even on raising the temperature to 1000° in vacuum.

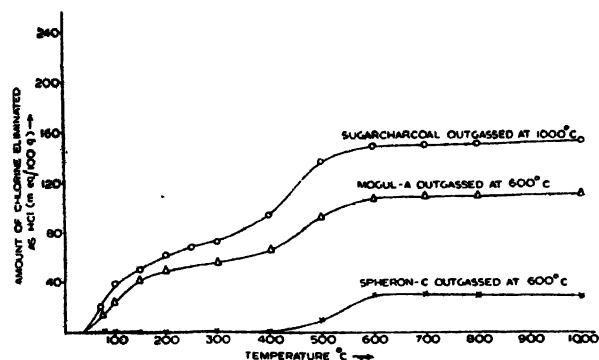


Fig.2. Elimination of chemisorbed chlorine as HCl on outgassing chlorinated carbons at different temperatures.

The elimination of chlorine as HCl in the case of Mogul-A and sugar charcoal which are known to be porous, however, commenced at a lower temperature, close to 70° and continued thereafter, although the rise in temperature had a gradually decreasing effect, as is evident from the decreasing slope of the graph

between 70° and 300°. At 300° there was again a spurt and the elimination proceeded at a relatively faster rate up to 600° beyond which, again, there was a levelling effect up to 1000°. It is observed that only about half of the chlorine chemisorbed by Mogul and less than half of the chlorine chemisorbed by sugar charcoal could be recovered as HCl even on evacuating the systems at 1000°. The rest of the chlorine remained intact even under these rather drastic conditions of desorption.

The data plotted in Figure 2 indicate not only high thermal stability of carbon-chlorine surface complexes formed at ordinary temperatures but also show that chlorine is chemisorbed at different sites of varying degrees of energies on placing carbons in contact with chlorine solution in carbon tetrachloride.

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