
QUARTERLY REVIEWS

THE CHEMISTRY OF CARBON-OXYGEN SURFACE COMPOUNDS

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In the many reviews of the preparation, properties, and structure of activated carbons and carbon blacks, little attention has been paid to the properties of the "carbon-oxygen complexes". Unless *very* special measures are taken to remove them, these complexes are in some degree present on the surface of every carbon used in the laboratory, or in commerce, and are often the source of the property by which the carbon becomes useful or effective. As might be inferred from a glance at the major sub-divisions of this Review, these complexes may often determine the adsorption, catalytic, and electrical properties of carbon; they act as intermediates in a variety of important reactions; they are vital in the compounding of rubber and the production of inks and paints; and they are important to the lubricating property of carbon.

The nature and quantity of the complexes which any given sample possesses are affected by its surface area, particle size, porosity, ash content, and degree of carbonisation and graphitisation, but in this Review an effort has been made to separate and minimise these effects in order to emphasise the intrinsic properties of the complexes themselves. This separation cannot always be done satisfactorily, especially with respect to earlier work, because substantial amounts of ash were usually present in the carbons. Also, in many cases no distinction is made between "high-temperature" carbons, whose oxygen lies almost entirely on the surface, and partially pyrolysed carbonaceous materials which have residual hydrogen and/or oxygen distributed throughout their bulk.

Mellitic anhydride, $C_{12}O_9$ (50% O), carbon suboxide polymer, $(C_3O_2)_x$ (47% O), and graphite oxide ($\sim 30\%$ O) are solids with reasonably well-defined properties and structure. This Review, however, is concerned primarily with carbon combined with 20% or less of oxygen in forms which are not well defined. Their existence was first reported¹ in 1812, and a few additional papers appeared later in that century, but the first systematic and comprehensive work² did not appear until 1913.

Formation and decomposition

Temperature is the most important factor which determines the nature and formation of the complexes by oxidising gases. If oxygen is added to

¹ de Saussure, *Annals of Philosophy*, 1815, 6, 241.

² Rhead and Wheeler, *J.*, 1913, 103, 461, 1210.

carbon at -78° or below, only physical adsorption occurs. Reaction with the surface sets in at higher temperatures, and the first amounts of oxygen are bound with no measurable pressure. Indeed, adsorption is so effective that traces of oxygen, nitric acid, and nitrogen dioxide can be removed from nitrogen by beds of activated charcoal at room temperature, or higher, making the nitrogen suitable for synthesis of ammonia or for analytical purposes. Oxygen-free hydrogen and inert gases can similarly be prepared.

Relative to the total oxygen-combining capacity of a carbon sample,³ only small amounts of oxygen are fixed at room temperature, but the amount increases with temperature until at $400-500^{\circ}$ carbons containing up to about 20% of oxygen may be prepared. These high-oxygen carbons are obtained with simultaneous formation of considerable amounts of carbon dioxide and monoxide. At still higher temperatures the amount converted into gaseous oxides increases and that converted into solid oxides steadily decreases; at 1000° there are virtually no surface oxides. This variation of composition with the temperature of oxidation of pure carbon is not the same as the variation with temperature of pyrolysis of cellulosic or hydrocarbon materials. In the pyrolysis process oxygen and hydrogen are eliminated from the bulk as well as the surface, and appreciable amounts of hydrogen are retained to much higher temperatures than is oxygen. Whatever the nature of the original carbons, the optimum temperature to fix large quantities of oxygen is $400-500^{\circ}$ with oxygen or nitrogen dioxide, and room temperature with ozone. Nitrous oxide, carbon dioxide and water are unsuitable for making high-oxygen carbons. Increasing particle size, degree of graphitisation and purity, and decreasing surface area all tend to decrease the rate of complex formation.

If large graphite crystallites are given a prolonged treatment with potassium chlorate in a solution of concentrated sulphuric and nitric acids, instead of an exposure to oxidising gases, graphite oxide is the principal product, with carbon dioxide and mellitic acid as common by-products. Graphite oxide may also be prepared by electrolysis of solutions of hydrofluoric, nitric, perchloric, sulphuric, or phosphoric acid, graphite being used as the anode. Gaseous oxygen is not produced in these electrolyses, but is instead held interlamellarly by the graphite, in what is often a highly swollen solid whose properties depend on the acid concentration. These solution treatments permit a separation of the graphite lamellæ and a substantial penetration by the oxidising agent, which are not possible with the gases. The peculiar structure and properties of graphite oxide which set it apart from other oxygen complexes arise from this basically different preparation procedure. Penetration of chemisorbed oxygen into the carbon (anode) lattice also occurs during the high temperature ($670-770^{\circ}$) electrolysis of alumina in molten cryolite.

³ Weller and Young, *J. Amer. Chem. Soc.*, 1948, **70**, 4155.

The main feature about the decomposition⁴ of the complexes is that, regardless of the source of carbon, the products are always oxides of carbon, with any hydrogen coming off as steam below about 700° and above that as hydrogen. Most of the hydrogen comes off above 900°. In general, surface oxides made at any temperature up to about 500° are thermally stable for long periods and under high vacuum at all temperatures below that at which they were made; regardless of the preparative method they are fairly stable up to about 300°. At the lowest decomposition temperatures the gas is largely carbon dioxide, and above 600° it is largely the monoxide—the ratio of the two gases changing continuously with temperature. Samples once heated to 1000–1200° will seldom show any but trace quantities of hydrogen in the decomposition products. When carbon suboxide polymer decomposes, the gaseous product is exclusively carbon dioxide below 100°, but at higher temperatures the monoxide is produced in increasing amounts. Graphite oxide decomposes to give carbon dioxide, steam, and small amounts of carbon monoxide. In both cases the solid product is an oxygen-complexed carbon which becomes graphite at high temperature.

Structure

The formulation of a structural theory of surface oxygen complexes which gives an unequivocal, integrated explanation of all the properties described in this Review is far from achievement. The principal functional groups which have been found^{5,6} by direct chemical analysis are $>C=O$, $-OH$ and $-CO\cdot OH$, with some evidence for a small number of ester groups; the difference (often as much as 75%) between total oxygen and that determined by functional-group analysis is usually assigned to "ether oxygen". The presence of these groups, as well as aromatic rings and C-H bonds, is also shown by infrared spectra. There is a great need for more information about the analytical behaviour of functional groups on large polynuclear aromatic molecules such as those which correspond to a graphite layer in a crystallite. The evidence already at hand with such model compounds shows that quinone, ketone, and phenol groups often do not react at all, or only partly react, with the standard reagents. There is also the question of specificity of reagent. Infrared spectra give only limited help because the wide absorption bands and high background absorption do not permit unequivocal assignment of frequencies, and there is usually more than one way to interpret changes in relative band intensities resulting from chemical treatment. Furthermore, carbons having more than about 94% of carbon are opaque to infrared, which in turn means that all infrared information has been obtained from coal, coal extracts, partially pyrolysed sugar, or highly oxidised blacks rather than from the surface complexes of relatively pure carbon.

⁴ Anderson and Emmett, *J. Phys. Chem.*, (a) 1947, **51**, 1308; (b) 1952, **56**, 753.

⁵ Studebaker, Huffman, Wolfe, and Nabors, *Ind. Eng. Chem.*, 1956, **48**, 162.

⁶ Blom, Edelhausen, and van Krevelen, *Fuel*, 1957, **36**, 135.

There seems to be no evidence for alcoholic hydroxyl groups. The separate determination of phenolic and hydroquinonic (quinolic) —OH is difficult, though a real advance was made in the recent development of a constant-potential coulometric method for hydroquinone (quinol) and quinone groups on blacks. Potentiometric titrations indicate that the acidic groups have a pK similar to that of phenol, and occasionally pK values similar to that of benzoic acid. The high-potential emission spectra of some carbon blacks showed the existence of twelve fragments in the discharge, and of interest here is the fact that in addition to considerable —OH and CO, there was a high concentration of CO_2^+ , which must have come from — CO_2H , and of —CHO which must have been originally associated in that form on the surface.

A number of carbon-oxygen structures have been proposed for which no direct experimental proof has been given. A recent example of this is a comprehensive theory⁷ which suggests that the acidic groups on the surface are primarily lactones and only to a small extent phenolic. Two types of lactone are postulated: (1) a fluorescein type which can form a sodium salt and be methylated, and (2) a "normal" (probably δ) type which can be hydrolysed by sodium hydroxide, but not methylated. The theory explains the properties of carbons with basic groups by postulating the presence of a benzopyran-benzopyrylium redox system.

Some specific chemical compounds have been removed from carbon surfaces, but their removal demonstrates an exceptionally limited type of chemical reaction with oxygen in the presence of the extractant (water), rather than proof of the existence of certain groups on the surface. For example, hydrogen peroxide is produced in very small amounts by oxygen in acid solution or by the combined action of oxygen and water vapour; and minute traces of oxalic acid can be repeatedly extracted with water from a given sample of ashless char. Diphenylene oxide, 2,6-xyleneol, and *p*-phenylphenol have been extracted in trace quantities from coals by pyridine and ethylenediamine, but they probably represent intermediate fragments in the coalification process rather than the surface complexes formed by oxygen or other oxidising agents.

Another approach to structure determination is to identify the degradation products resulting from oxidative methods, and then to deduce from these what the parent compounds must have been. In the main, however, such studies substantiate the graphitic nature of coals but give no specific information about the surface complexes.

High-temperature phenomena such as combustion probably do not depend so much on the properties of specific surface structures, which would tend to be unstable at these temperatures, as they do on mobility of oxygen atoms, interlamellar penetration, and lattice properties.

Graphite oxide (GO) has a controversial formula $[(C_6O_2H)_x, (C_7O_4H_2)_x, (C_8O_4H_2)_2]$ and many properties in common with the carbon-oxygen

⁷ Garten and Weiss, *Rev. Pure Appl. Chem.*, 1957, 7, 69.

surface complexes of chars and blacks with high percentages of oxygen. In spite of the compounds' having a "formula", these properties are retained on thermal decomposition over a composition range of 40—18% without significant change in *X*-ray structure, and even down to low percentages of oxygen as the GO structure collapses. The chief difference between GO and the other oxygenated carbons is that GO has a high concentration of oxygen-containing groups attached interlamellarly in the relatively easily accessible space (6.2 Å) between the carbon planes. The interplanar distance in graphite is 3.44 Å.

There is general agreement⁸ that hydroxyl is one of the major groups attached to carbon in GO, and it appears that some hydroxyl groups are involved in a keto-enol equilibrium. The remaining oxygen atoms are believed to be attached to "meta-oxygen" bridges (*i.e.*, oxygen attached to the first and third of a chain of three carbon atoms) which are randomly distributed both above and below each carbon layer. There are a few carboxyl groups, probably on the periphery of the GO layers. The carbon layers themselves are puckered rings, unlike the planar aromatic layers of graphite crystallites. Controlled thermal decomposition first eliminates the *meta*-oxygen bridges as carbon oxides. Finally, at 130—180° the hydroxyl groups are eliminated with concomitant collapse of the *c*-spacing and disappearance of swelling properties. Rapid heating to 200° causes GO to explode and produce exfoliated carbon, exceedingly thin wafers of graphite carbon containing 20% of oxygen.

Selected oxidation reactions

Combustion of Carbon.—In spite of a long history of intensive research on the combustion of carbon, there is still no comprehensive theory which satisfactorily accounts for all of the kinetic, structural, catalytic, and temperature-effect data which have accumulated. The major facts,⁹ which have been established under conditions which exclude secondary production of carbon dioxide by carbon and oxidation of the monoxide by oxygen, indicate that the primary step in the combustion of pure carbon is dissociative adsorption of oxygen to give oxygen complexes. Below about 500° the rate of formation of these complexes is greater than their rate of decomposition, but as the temperature of combustion increases, these complexes become increasingly unstable and reactive, and the composition of the primary decomposition products (CO and CO₂) alters to become predominantly CO, especially above 1000°. The two oxygen atoms in the dioxide come from different oxygen molecules; thus appreciable formation of carbon dioxide requires a low enough temperature to permit a significant surface concentration of oxygen complexes for reaction with oxygen. At high temperatures the mobility of oxygen atoms no doubt plays a part, and at still higher temperatures (of the order of

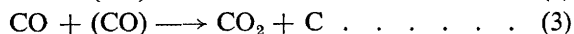
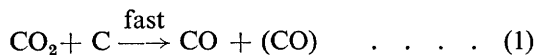
⁸ Claus, Plass, Boehm, and Hofmann, *Z. anorg. Chem.*, 1957, **291**, 205.

⁹ Rossberg, *Z. Elektrochem.*, 1956, **60**, 952.

2100°) self-diffusion of carbon atoms and increase in degree of graphitisation set in. Since experimental conditions or the nature or quantity of the sample may also superimpose diffusion processes, secondary reactions, and varying surface areas, it is no wonder that the kinetics of this "simple" reaction have not been completely elucidated even for pure carbon. A rate equation, derived recently¹⁰ to describe the oxidation of carbon *filaments*, takes account of most of these variables and reasonably assumes the presence of reactive hydrogen atoms throughout the lattice as major impurity sites, but it makes no guess as to the structure of the oxygen or hydrogen complexes. Most of the detailed oxidation mechanisms are oversimplified and postulate attack on prism faces of the crystallites, at edge atoms of the layer planes, and assume functional group reactivities characteristic of relatively simple organic molecules. There is evidence, however, that the base-plane atoms of the crystallites also have strong binding and reactivity. High-temperature experiments indicate that it is the disorganised carbon atoms and the smallest crystallites which first disappear, partly through reaction with oxygen and partly through formation of large crystallites; when a base plane disappears it does so all at once. Crystallite diameters and gross particle sizes stay remarkably constant through the major part of combustion.

Combustion is exceedingly sensitive to catalytic impurities, the most effective being potassium and sodium oxides and carbonates. The principal effects are increase in rate, an increase in the relative amount of carbon dioxide produced, and change in the order of reaction. Mercury vapour (from manometer, etc.) has a similar effect. Water vapour catalyses the combustion, but has little effect on the CO/CO₂ ratio. Traces of halogen-containing vapours (phosphoryl chloride, carbon tetrachloride, and chlorine) retard the decomposition of the complexes, but do simplify such studies by preventing the secondary oxidation of carbon monoxide.

Oxidation by Carbon Dioxide.—Carbon dioxide oxidises carbon to the monoxide by a relatively simple mechanism, with oxygen complexes (CO) as intermediates.¹¹ The steps are:



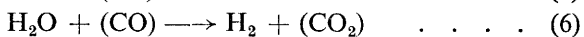
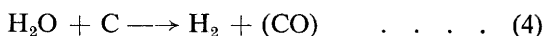
Diffusion processes being excluded, the reason that the mechanism is not more complicated is probably that the dioxide does not react appreciably below 600°, and hence it is not possible to form those low-temperature

¹⁰ Blyholder, Binford, and Eyring, *J. Phys. Chem.*, 1958, **62**, 263.

¹¹ Reif, *J. Phys. Chem.*, 1952, **56**, 778.

complexes which yield carbon dioxide on decomposition; further, free oxygen is not involved. A side reaction which plays no significant rôle in the oxidation is the exchange of carbon atoms between the dioxide and the carbon lattice, but not with carbon monoxide. The temperature must be greater than 700°, and at 1600° a really significant exchange takes place. Potassium, sodium, and iron oxides are excellent catalysts.

Steam-Carbon Reaction.—It cannot be said that the mechanism of this reaction is completely established beyond doubt, but the evidence^{12,13} available strongly suggests the existence of two surface complex intermediates which might be designated as the "CO-complex", (CO), and the "CO₂-complex", (CO₂). The postulated mechanism steps are:



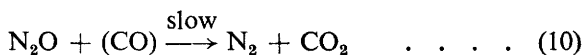
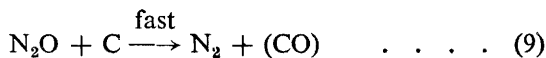
At low temperatures, only steps 4, 6, and 7 are important because the "CO-complex" is thermally stable and unreactive towards hydrogen. At temperatures of about 600—1400°, all steps are important in a closed system or in a system with appreciable added or accumulated partial pressure of hydrogen; in a fast-flow system or under conditions where hydrogen cannot accumulate, step 8 is unimportant; at very low partial pressures of steam in a flow system, only steps 4 and 5 are important. At high temperatures (above 1400°) only steps 4, 5, and 8 are important because the very rapid decomposition of the "CO-complex" leaves little opportunity for 6 and 7 to occur; 8 is again unimportant under conditions of low partial pressure of hydrogen.

The steam-carbon reaction is exceptionally sensitive to catalytic impurities such as potassium, sodium, iron, and copper oxides: the order of the reaction may be changed, and with very large amounts of potassium carbonate the whole nature of the reaction is changed so that hydrogen and carbon dioxide are the main products, along with an appreciable amount of methane. The large increase in carbon dioxide may be due largely to the CO-H₂O reaction, especially when diffusion is important. As steam pressures rise from 1 to 50 atm. in the range of 750—850°, there is a rapid increase in methane production. The mechanism of this competing reaction is still in doubt. Complexes are probably involved only if methane is made by the direct action of water on partially hydrogenated carbons, and not if by direct action with hydrogen.

Oxidation by Nitrous Oxide.—The oxidation of carbon by nitrous oxide proceeds by a very simple mechanism:

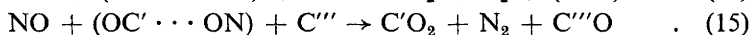
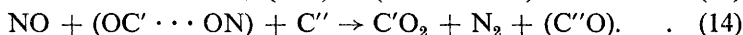
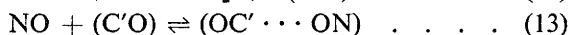
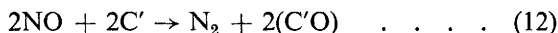
¹² Singh, Parkash, and Puri, *Chem. and Ind.*, 1959, 18.

¹³ Wicke and Rossberg, *Z. Elektrochem.*, 1953, 57, 641.



Only step 9 occurs at low temperatures and the reaction stops as soon as all reactive sites have been converted into oxygen complexes. Reaction at 0° has been reported, but normally 100–300° is required. Step 10 sets in at some intermediate temperature, and the production of carbon dioxide is a first-order reaction in the range 300–700°. With a filament and low nitrous oxide pressure at high temperatures (900–2000°) there is small probability that nitrous oxide will react with a complex whose concentration is very low because of rapid thermal decomposition, and consequently carbon monoxide is the principal product, with only traces of the dioxide. As in the other oxidations, ash acts catalytically.

Oxidation by Nitric Oxide.—The mechanism for this oxidation is:



Below 200° only step 12 occurs, and this ceases when the reaction sites have been covered with complexes. Step 13 involves the reversible physical adsorption of nitric oxide at the oxygen complex sites, and the (C''O) complexes formed at C'' adjacent to C' can serve as adsorption sites in 13. After providing oxygen complexes at the outset of a reaction, when there are no oxygen complexes, the rôle of step 12 is to replenish those complex sites not regenerated in step 15. Step 15 is minor compared to step 14, contributing about 8% at 450° or 20% at 600°. The steady-state concentration of the complex decreases with increasing temperature. Ash acts catalytically.

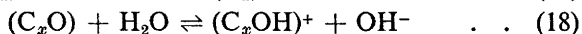
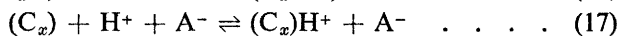
Oxidation by Bacteria.—It has been neatly demonstrated that certain soil bacteria will, at room temperature in the presence of sterile carbon dioxide-free air, oxidise chars or blacks that have been pyrolysed at 1200°. The ash was not removed, and the water vapour needed to preserve the bacteria may have participated in the oxidation process. The rate more than doubled from 20° to 40°; the bacteria died at 100°. No test was made for the presence of surface complexes or for whether the bacteria actually attacked complexes rather than bare carbon atoms, but both seem very likely.

Adsorption of electrolytes

Adsorption of electrolytes varies tremendously with the nature and amount of the surface-oxygen complexes. Ash-free carbons outgassed at

1000° and subsequently exposed to oxygen at temperatures below about 200° or above about 750° will adsorb strong acid from solution, but no strong base. The same carbons heated in oxygen in the range 200—750° will adsorb strong base but no strong acid. The optimum temperature of oxygen-treatment for base adsorption is about 400—500°, the same temperatures as for the maximum production of surface oxides. There is, however, no clean-cut temperature boundary between acid and base adsorption, but instead a certain overlap where one drops off and the other begins. Carbons made by low-temperature carbonisation adsorb base only, the amount decreasing as the temperature is raised from 500° to 750°, whereat acid adsorption sets in. If the acid and base adsorbing capacities of a given carbon are compared under conditions for optimum adsorption of each, base adsorption is found to be far greater than acid adsorption. The many and diverging views of electrolyte adsorption were clearly summarised¹⁴ in detail in 1944. With the additional research reported since then, it appears that the picture presented below satisfactorily explains the published data.

Acid-adsorbing Carbons.—Adsorbates on these carbons may be classified in the order of decreasing adsorbability: (a) non-electrolytes, (b) large ions of organic strong electrolytes, (c) hydrogen ions on oxygen complexes, (d) hydrogen ions on bare carbon, and (e) metal ions, inorganic anions, and hydroxyl ions (these last can be held only in the diffuse double layer). The following equilibrium expressions, using these relative adsorbabilities, will explain the adsorption phenomena.

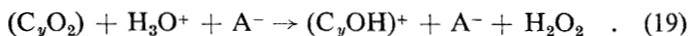


The electrokinetic potential of the carbons (parentetic entities on the right) is positive, as shown. (C_xO) appears to be quinonic in nature. Equilibrium 16, observed only in dilute solution ($< 0.02N$), has been confirmed by experiments which show, up to a point, a 1:1 correspondence between surface oxygen atoms and adsorbed acid; if there are no oxygen atoms, there is no adsorption. At higher acid concentration, adsorption by step 16 still takes place, but is masked by the larger additional adsorption of step 17, which varies with concentration according to a Langmuir-type expression. The acid adsorbed by step 17 is easily washed out with water, but that held by step 16 cannot be washed out—it must be removed with sodium hydroxide, the excess of which is easily washed out with water. The anions held in the diffuse double layer are easily exchangeable for other anions from neutral salts. The primarily-held hydrogen ion may be displaced by cations of strong organic bases such as methylene-blue

¹⁴ Steenberg, "Adsorption and Exchange of Ions on Activated Charcoal", Almquist and Wiksells, Uppsala, 1944.

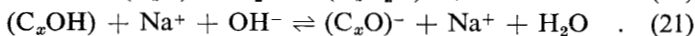
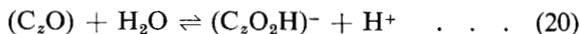
cation, leaving A^- exchangeable. If the primarily-held hydrogen ion is displaced by anions of strong organic acids (picrate) it is the positive ions which become exchangeable. Equilibrium 18 explains why aqueous suspensions of the carbons are alkaline, though only slightly so because most of the hydroxyl ions are held in the diffuse double layer. When the carbons are suspended in solutions of neutral salts, the solution becomes appreciably basic because the hydroxyl ion goes into solution by anionic exchange.

The surface oxygen complexes involved in steps 16 and 18 may be formed before acid adsorption measurements or simultaneously with them. If the adsorption is performed in air so that gaseous oxygen as well as acid is available, another type of complex (C_yO_2) can be formed which leads to the production of small amounts of hydrogen peroxide, as follows:



If a carbon is used which has no surface oxygen, the initial amounts of gaseous oxygen are used to form (C_xO), which does not lead to hydrogen peroxide formation. The amount of peroxide produced is equivalent to less than 10% of the acid adsorbed in step 16.

Base-adsorbing Carbons.—These carbons have a negative electrokinetic potential, and their aqueous suspensions are acidic. It is not possible to wash out most of the adsorbed base with water, and large amounts of non-electrolytes can be added without affecting the adsorption of base. They have cation-exchange properties, but with less capacity than for base adsorption. These properties may be accounted for by equilibria involving two types of site: (C_xOH) being hydroquinonic (quinolic) or phenolic in nature, and (C_xO) of the nature of an acid anhydride or fluorescein lactone. (C_xOH) may be made by reduction of (C_xOH)⁺.



Equilibrium 20 accounts for the slight acidity of aqueous suspensions, only slight because most of the hydrogen ion is held in the diffuse double layer. The hydrogen ion may be exchanged for sodium ion from sodium acetate, as is commonly done for analytical purposes. If it is exchanged for sodium ion in sodium hydroxide, then the total base adsorption is determined by both types of complex; this is also done for analytical purposes. Graphite oxide also has pronounced cation-exchange properties.

The behaviour of large organic strong-electrolyte ions is not clear, but it is certain that they are involved in both primary and exchange adsorption, and that the complexes can cause an enormous increase in adsorption for no change in area. This sensitivity of ionic dyes to oxygen complexes as well as to pore size makes them unsatisfactory for measurement of surface area.

Adsorption of non-electrolytes

In general, surface oxygen complexes have no effect on the physical adsorption of non-polar gases. Nevertheless, the complexes have been known to cause errors in interpretation of physical adsorption data. For example, even though the charcoal samples had been outgassed at 300° *in vacuo*, low-pressure adsorption of carbon tetrachloride (less than 0.01 mm.) was shown to displace part of the complexes as oxides of carbon and to provide a gas pressure of these oxides comparable to the carbon tetrachloride pressure. Chlorobenzene, hydrogen chloride, and silicon tetrafluoride will do the same, as will, doubtless, many other gases not proved to do so. Such chemical displacement is not an effective method for removal of complexes. Certain oxidising gases which form complexes on adsorption may also yield misleading data. Thus, the "adsorption" of nitric oxide on carbon liberates nitrogen, leaving the oxygen on the surface, and leads to quite erroneous conclusions if the assumption is made that the equilibrium gas pressure is nitric oxide.

The adsorption of polar gases on carbon is usually seriously affected by oxygen complexes. The adsorption of H_2O , $\text{CH}_3\cdot\text{OH}$, NH_3 , $\text{CH}_3\cdot\text{NH}_2$, SO_2 , CO_2 and HCl is greatly increased, and though these gases are thus unreliable for surface area measurements, they may be useful for characterising the polar sites on a carbon surface. Sulphur dioxide is especially recommended for this. Certain of these gases have special peculiarities. Ammonia and methylamine are adsorbed so abnormally that it has been suggested that perhaps they dissolve in the surface oxides or form a salt; they are desorbed at pressures lower than that at which they were adsorbed. At 200° or above, ammonia will react with surface oxides to give surface nitrogen compounds (possibly amides) which are stable to above 400° . Sulphur dioxide on chars, in the presence of oxygen, forms such a stable complex that it cannot be desorbed up to 220° , and then only as the trioxide—in fact, it serves as a basis for a method of making sulphuric acid.

Water,¹⁵ being carbophobic, is negligibly adsorbed on pure carbon at low pressures, P . If the carbon is non-porous, adsorption rises sharply when $P > 0.9P_0$ and ceases at P_0 (vapour pressure of pure liquid) with something like two statistical layers, instead of the thirty or more which would have been expected with a non-polar vapour. If the carbon is porous, adsorption rises sharply when P reaches about $0.5\text{--}0.6P_0$ and then remains fairly constant up to P_0 with an adsorbed *liquid* volume of water very nearly the same as that for a non-polar vapour. The effect of oxygen complexes (or ash!) on these isotherms¹⁶ is to increase adsorption at low pressures, to shift the rapid rise of adsorption to lower pressures, and to increase the total adsorption at P_0 . Up to the beginning of the rapid rise there is a 1:1 correspondence between chemisorbed oxygen atoms and

¹⁵ Pierce, Smith, Wiley, and Cordes, *J. Amer. Chem. Soc.*, 1951, 73, 4551.

¹⁶ Dubinin and Zaverina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 594.

adsorbed molecules. Because of strong water-water interaction, additional adsorption occurs on these oxygen-atom sites, and this leads to "island" formation rather than to "monolayer" formation. This island formation, which is peculiar to water on carbon, provides a situation in which the adsorption process is different from the desorption process.^{17,18} Thus, in the case of porous carbons the capillaries are filled by coalescence of islands, but they empty from menisci; and desorption from non-porous carbons is from large islands which were formed on adsorption by coalescence of small ones. Water held in capillaries, or in large islands over several polar sites, is held more strongly than in small islands over one polar site, and lower pressure is needed for desorption. As a consequence, water desorption curves always lie to the left of the adsorption curves at pressures above those needed to adsorb one water molecule on every chemisorbed oxygen atom.

Adsorption of water by graphite oxide is a very slow interlamellar process and several weeks are needed to attain equilibrium at each pressure. Interlamellar spacing is 6.2 Å for 0-4% of water, 6.8 Å at 11% of water, and approximately 11 Å with 60% or more. Desorption is also slow, and removal of the last traces of water is almost impossible.

The adsorption of many common non-electrolytes from solution is affected by the presence of the oxygen complexes. Three of these are worthy of special comment. Iodine has been widely used for surface-area determinations because of simplicity in analytical determination, but data from many sources indicate that oxygen complexes severely decrease iodine adsorbed either from water or from organic solvents and render this method unsatisfactory for area measurements. A standard measurement involving the adsorption of diphenylguanidine (an accelerator in rubber manufacture) from benzene is commonly used as a sensitive measure of the amount of surface oxygen. Recent experiments in which different surface groups were chemically blocked indicate that the surface carbonyl group is primarily responsible for diphenylguanidine adsorption. Toluene and benzene are selectively adsorbed from heptane solution if complexes are on the surface, and essentially the reverse is true without the complexes. It is judged that this behaviour is caused by the strong interaction of the π electrons of aromatic nuclei with the "acidic complex", in a manner similar to the interaction with silica gel.

Graphite oxide can reversibly adsorb polar molecules either from pure liquid or from hydrocarbon solution. Dioxan can form either one or two flatly oriented layers between carbon planes, giving rise to lamellar separations of 9.8 or 14.5 Å. In the homologous series of alcohols the swelling is about constant up to propanol, then becomes increasingly large with butanol, pentanol, etc., indicating a change from "flat" to "upright" orientation.

¹⁷ Pierce and Smith, *J. Phys. Colloid Chem.*, 1950, **54**, 784.

¹⁸ Dubinin, Zaverina, and Serpinsky, *J.*, 1955, 1760.

Catalytic activity

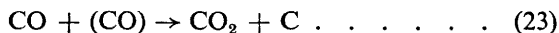
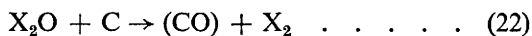
Reactions involving Oxygen.—In most cases of carbon-catalysed air oxidation it has not been explicitly demonstrated that surface oxygen complexes participate in the oxidation. In the case of $\text{Fe}(\text{CN})_6^{4-}$, NO_2^- , AsO_3^- , Sn^{2+} , and quinol, it has been shown¹⁹ that the maximum activity is observed with carbons with maximum amounts of oxygen, and it is likely that the complexes are involved with all examples reported here.

(a) Organic compounds catalytically oxidised in aqueous solution are: amines, amino-acids, anilines, *N*-substituted anilines, and aminophenol; formic, oxalic, malonic, and thioglycollic acids; salts of uric and substituted uric acids in alkaline solution; thiourea and phenylurea; quinol; allantoin; hexosephosphoric acid. Catalysis may be promoted by ash, especially by the Fe-C-N linkage. Cyanide and thiocyanate ions eliminate the promoted catalysis of iron, and pentyl alcohol and urethanes inhibit by desorbing the species to be oxidised. It appears that hydrogen peroxide is not an intermediate because the presence of potassium iodide has no effect on the velocity. Compounds not oxidised are: ethanol, amine hydrochlorides, fatty acids, carbohydrates, xanthine, hypoxanthine, caffeine, and theobromine.

(b) Inorganic substances or ions catalytically oxidised in alkaline solution are: I^- , S^{2-} , SO_3^{2-} , NO_2^- , SnO_2^{2-} , CrO_3^{3-} , AsO_3^{3-} , $\text{Fe}(\text{CN})_6^{4-}$, N_2H_4 . In acid solution: Sn^{2+} , Fe^{2+} , Hg_2^{2+} , I^- , $\text{Fe}(\text{CN})_6^{4-}$, SO_2 , H_2S .

(c) The oxidation of nitric oxide at room temperature and of sulphur dioxide from room temperature up to 200° is strongly catalysed, and there is qualitative evidence for the catalytic oxidation of ethylene, propene, and ethanol vapours.

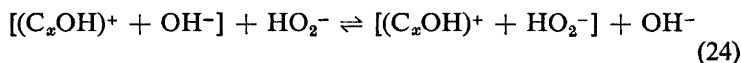
Reactions which do not involve Oxygen.—(a) The oxidation of CO by H_2O , N_2O , and NO proceeds in each case through a surface oxide. For H_2O and N_2O (represented as X_2O), the mechanism is:



The mechanism for NO has not yet been worked out.

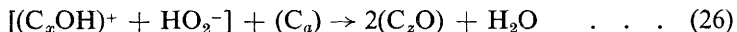
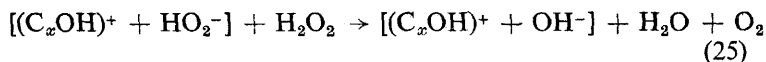
(b) The reaction of hydrogen with bromine at 150°, used as a simple measure of "catalytic activity" of carbons, is inhibited by the complexes.

(c) The following ion-exchange mechanism²⁰ accounts for most of the facts known about the hydrogen peroxide decomposition:



¹⁹ King, *J.*, 1936, 1688.

²⁰ von Brinkmann, *Kolloid Z.*, 1951, 123, 116.



Decomposition is rapid in basic solution where the chain steps 24 and 25 are favoured by having HO_2^- in reasonable concentration and by having a carbon with a large number of basic groups (C_xO) on the surface. Decomposition is slow in acid solution where HO_2^- concentration is very low and equilibrium 16, not 24, is favoured. Step 26 accounts for the observation that when carbons catalyse the decomposition of hydrogen peroxide, their acid-adsorbing capacity decreases, and their base-adsorbing capacity increases by an amount which is at least double the loss in acid-adsorbing capacity. Step 26, being a chain-breaker, stops catalysis and accounts for the fact that eventually a catalysing carbon is virtually unable to effect further catalysis. If at the outset, hydrogen peroxide creates a few new (C_xO) sites by direct action on the carbon, the apparent increase in rate constant with the peroxide concentration is explained. At elevated temperatures carbon dioxide is also produced, being in excess of oxygen in dilute solution. Carbons made from nitrogen compounds give immeasurably fast action, and physically adsorbed gelatin inhibits catalysis.

(d) Para-hydrogen is usually produced by conversion from ortho-hydrogen in the presence of suitable charcoals at liquid-air temperature. Recent work²¹ shows that the best charcoals for this purpose are prepared by carbonising sugar (or other cellulosic compounds) at about 600° to give a char containing 90–94% of carbon. The oxygen in this product cannot be considered to be primarily in the surface or involved in the para-ortho conversion. Instead, paramagnetic resonance studies have shown that such a carbon possesses the maximum concentration of free radicals, caused most probably by the presence of large condensed resonating ring structures with unsaturated edge bonds and stabilised unpaired electrons. The para-ortho conversion involving a paramagnetic mechanism is improved by the presence of paramagnetic oxygen physically adsorbed at liquid-air temperatures, but oxygen adsorbed above -80° eliminates the paramagnetic centres (and conversion ability) because each oxygen molecule shares a pair of electrons with a charcoal free radical. Two pairs of electrons are probably not shared by one oxygen molecule because of the low radical concentration; instead, it is thought that a stabilised peroxidic complex, $-R-O-O\cdot$, is formed which is incapable of effecting the para-ortho conversion.

(e) The carbon-catalysed hydrogen-deuterium exchange reaction at 50° is inhibited by the oxygen in and on the carbon, for catalytic activity increases with carbonising temperature from zero at 650° to high activity at 950°. The effect of surface oxygen alone has not been published. It is postulated that a pool of interacting electrons is needed for catalysis here,

²¹ Turkevich and Laroche, *Z. phys. Chem. (Frankfurt)*, 1958, **15**, 399.

rather than individual non-interacting electrons as in the case of ortho-para conversion.

Thermodynamic properties

Chemisorption.—The first quantities of oxygen admitted to a carbon surface at room temperature are chemisorbed with exceedingly high heats of formation (70—100 kcal./mole), of the same order of magnitude as the heat of formation of carbon dioxide. These heats decrease rapidly as additional oxygen is added, finally levelling out at about 5.5—6.0 kcal./mole when physical adsorption sets in. Nitric acid appears to have a very high heat of adsorption (~ 70 kcal./mole) for the initial amounts, but this has been shown to be the heat of the reaction which forms nitrogen gas and surface complexes. However, whether made by nitric oxide or by oxygen, the initial heat of formation of the complex is about 40 kcal. per g.-atom of oxygen. The heat of formation of complexes made at 400° (calculated from heats of combustion) is ~ 32.5 kcal. per g.-atom of oxygen, independent of the amount of oxygen combined. The stability of these 400° complexes is thus almost as great as that of the small initial quantities adsorbed at room temperature, and vastly greater than that of the bulk of the oxygen adsorbed at room temperature. In contrast to this, the heat of combustion of graphite oxide varies only from 92 to 94.1 kcal. per g.-atom of carbon even though the oxygen content may vary from 0 to 30%. This heat of combustion, almost identical with that for graphite, indicates the very weak oxygen binding in graphite oxide and is in keeping with its unstable and explosive nature.

Physical Adsorption.—Direct calorimetric measurement²² of the integral heats of adsorption of NH_3 , $\text{CH}_3\text{-NH}_2$, CO_2 , and SO_2 on carbon blacks indicates that these gases have a high initial heat of adsorption if the surface has oxygen complexes. With increasing coverage the heats for the last two fall steadily and approach the heat of liquefaction. Ammonia, however, after an initial sharp drop, continues to have a high heat, about 3 kcal./mole greater than the heat of liquefaction, independent of coverage in the region studied. In general, the heat of adsorption of non-polar gases is unaffected by the presence of complexes.

Because the adsorption of water on carbon is small and accompanied by very small heat effects, direct calorimetry is not very reliable and heats of adsorption must be determined indirectly. The common method of determining isosteric (differential) heats of adsorption by calculation from adsorption isotherms obtained at two temperatures has been applied to water, and has led to conflicting conclusions as to whether more or less heat is liberated on adsorption than in condensation on bulk water. The very small amount of adsorption, the continual reaction of water with the surface causing an increase in surface polarity during the course of isotherm measurements, and the inapplicability of the Clausius-Clapeyron

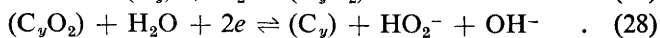
²² Spencer, Amberg, and Beebe, *J. Phys. Chem.*, 1958, **62**, 719.

equation under these conditions contribute to this difficulty. A more reliable method combines heat of immersion measurements with one adsorption isotherm, and it shows that the first amounts of water vapour adsorbed at low pressure are adsorbed with less than the heat of condensation to pure liquid. Spontaneous adsorption of this nature is possible here because a compensating increase in entropy of the adsorbed film over that of the corresponding pure water is provided by the practically complete isolation of the oxygen-complex adsorption sites. The heat of immersion in water and methanol is a linear function of the number of oxygen atoms,²³ in agreement with the 1:1 correspondence of oxygen atoms with adsorbed water molecules in the low-pressure regions. There is also a direct relation between the heat of immersion and the adsorbability of baryta, and also the quantity of oxygen that can be removed as carbon dioxide. Oxygen which may be evolved as carbon monoxide or water appears to be unrelated to the heat of immersion. Adsorption of water by graphite oxide involves the additional factor of swelling, the heat of which has been judged to be very small.

The heat of adsorption of inorganic bases from solution on to ash-free charcoals previously wet with water corresponds in magnitude to the heat of neutralisation of carbonic acid by the respective bases.

Electrical properties

Oxygen Electrode.—The only known reversible oxygen gas electrode at room temperature involves carbon as the conducting solid. This was first discovered in 1943 when it was shown that the reversible reaction requires the presence of OH⁻ and HO₂⁻ in solution. Measurements of magnetic susceptibility and of electron paramagnetic resonance indicate that the oxygen so involved may be adsorbed as a peroxidic complex (C_yO₂). This is further substantiated by recent work²⁴ with ¹⁸O, which shows that none of the hydrogen peroxide involved in the reversible electrode reaction involves the breaking of the O—O bond. Thus, the electrode reaction is probably



It is likely that step 28 is composed of two one-electron steps involving an adsorbed HO₂[·] radical as intermediate. A certain similarity of this mechanism to equation 19 for hydrogen peroxide formation, or to the mechanism for catalysed hydrogen peroxide decomposition, is at once evident, but carbons used for reversible electrode work have negligible area and are probably unable to show the other two effects.

Electrical Resistances.—Carbon-carbon contact resistance under low

²³ Kraus, *J. Phys. Chem.*, 1955, **59**, 343.

²⁴ Davies, Clark, Yeager, and Hovorka, *J. Electrochem. Soc.*, 1959, **106**, 56.

weight loads is not affected by simple evacuation. High-temperature evacuation removes the oxygen complexes and lowers the resistance for a 1 mg. load by about 75%, but for loads greater than 100 mg. the contact resistance is virtually unaffected; 10^{-4} mm. of O_2 will raise the contact resistance again.

In general, oxygen complexes increase the electrical resistance of carbon, but they do not seem to interfere with the slight decrease in electrical resistance usually caused by the physical adsorption of other gases. A careful study²⁵ of the variation of the bulk electrical resistance with surface oxygen showed that a fairly sharp maximum in resistance occurs with a thoroughly outgassed (at 1200°) powdered carbon when it is re-oxidised in the temperature range of 500 — 700° , near the optimum range for forming large amounts of complexes. This maximum, amounting to about a 1000-fold increase in resistance, corresponded to about 4% of oxygen. Addition of oxygen at 20° to a well-outgassed carbon filament causes an increase of resistance of a few units % over a period of several days, but if the oxygen is added at a high temperature (1000 — 1200°) an immediate increase in resistance of about 25% is observed. Both the filament and the powder work indicate that part of the effect of oxygen is produced by interlamellar penetration of oxygen.

It is noteworthy that in the case of graphite oxide, where almost all of the oxygen is interlamellar, a tremendous drop in resistance occurs on slow thermal decomposition as the oxygen content goes from 24% to 22%, though there is no significant change in interlamellar spacing.

Miscellaneous.—Oxygen complexes formed by adding oxygen to outgassed carbon also cause an immediate large rise in the surface potential which subsequently disappears during several hours. In addition, 10^{-2} mm. of oxygen will cause a 50% reduction in the ultraviolet photoelectric sensitivity of carbon.

Rubber

About 95% of the total carbon black production (approximately 2.2×10^9 lb. in 1957) is used as a filler for rubber products. Such products, to be satisfactory, require a strong bond between the black and the rubber polymer. Surface oxygen complexes play an important rôle in this binding and to a certain extent determine the preparation and properties of the final product. Thus, blacks with a high concentration of surface oxygen will yield a rubber product which ages more rapidly and has a higher electrical resistance, and a mix which has a longer "scorch time" (induction period for premature vulcanisation) than those with low concentration of surface oxygen.

The complexes have a profound retarding effect²⁶ on the rate of "cure"

²⁵ Hirabayashi and Toyoda, *Tanso*, 1954, 4, 2.

²⁶ Cines, *Rubber Age*, 1951, 69, 183.

(vulcanisation). If, for a given formulation, all variables are held constant except for the proportion of surface oxygen, the resulting rubber product is observed to be increasingly poor with respect to mechanical tests such as tensile strength, stretching modulus, and abrasion resistance with increasing content of surface oxygen. Primarily, this decrease in quality of product indicates only an increasingly poor state of vulcanisation, and if in each case the accelerator concentration is adjusted so as to give the same state of cure for a given cure-time, the mechanical test results from the product seem to be essentially independent of the state of oxidation of the black.

The nature of the binding between carbon particles and polymer is not at all well known. Some relevant experimental facts which must be considered are: (a) dihydromyrcene (a diolefin) is adsorbed at 100° on a channel black (3–5% of oxygen) with polymerisation and a high heat of adsorption, whereas only reversible adsorption without polymerisation occurs on the same black without oxygen complexes; (b) but-1-ene is isomerised to *cis*-but-2-ene at temperatures greater than about 100° on a channel black (3% of oxygen) but not on the same black without oxygen; (c) butadiene eliminates the “—OH wave”, and 2,2,4-trimethylpentane eliminates the “quinone wave” observed in polarographic examination of oxidised blacks; (d) the rate of binding increases with the concentration of olefin bonds in the polymer; (e) blacks with oxygen complexes react much more rapidly in polymer formation than if the oxygen is not present; (f) spontaneous gelation accompanied by carbon–polymer bonding occurs when a styrene partially polymerised by oxygen is suddenly mixed with a black; (g) diphenylguanidine and a number of other accelerators are preferentially adsorbed on oxygen complexes.

One recent hypothesis²⁷ of carbon–rubber binding postulates the presence of adjacent —OH and >C=O groups on the surface and suggests the transfer of a hydrogen ion from a hydroxyl group to a double bond of the elastomer, leaving a negative charge on the carbon particle and creating a carbonium ion of the elastomer. This carbonium ion may then attack the aromatic ring and bind the elastomer to the carbon particle by a C–C bond, or it may attack a quinone group and bind the elastomer by a C–O–C bond. If the binding does not come from the double bond, it is suggested that the quinone group abstracts a hydrogen atom from the most substituted carbon of a saturated elastomer chain, forming a hydroxyl group on the carbon particle and creating a free radical of the elastomer. The resulting elastomer radical would then attack the aromatic ring and establish a C–C bond to the particle by alkylation.

Pigments

About 2.5% of the total production of carbon black is used by manufacturers of printing ink. The “long-flow” pigments²⁸ are channel blacks,

²⁷ Hallum and Drushel, *J. Phys. Chem.*, 1958, **62**, 110.

²⁸ Drogin, *Amer. Ink Maker*, 1952, **30**, 30.

partly characterised as small, soft particles with moderate areas and a "percent volatile" (weight loss on heating, primarily as carbon oxides) of about 5—15%. These pigments make an ink which is finely dispersed, spreads rapidly, distributes evenly, and is non-wearing on plates. The large quantity of oxygen complexes retards drying and makes it necessary to add driers to these inks. Furnace pigment blacks have larger, harder, more abrasive particles with smaller areas and less "percent volatile"; they are more easily handled. The surface concentration of oxygen complexes is comparable on the two types, and they are the key to the stability of the pigment suspensions. These factors involving flow and suspension stability in inks must also be considered in the formulation of paints and varnishes.

Friction

Experimental evidence is against the popular view that the most important factor in the lubricating properties of graphite is the slippage permitted by the relatively weak van der Waals forces between internal cleavage planes. If any form of carbon (including diamond) is heated to 1200° *in vacuo*, there is an enormous increase in friction at the carbon-carbon contact under slow-moving loads carried at room temperature in a vacuum. Subsequent addition of oxygen or water vapour at pressures of 0.1 mm. or less will immediately cause a great decrease in friction. It is now believed²⁹ that the oxygen complexes reduce the friction between the individual crystallites, rather than between cleavage planes, and that on high-temperature evacuation the loss of oxygen from the crystallite surfaces leaves free valencies available to increase adhesion between neighbouring crystallites. Physical adsorption of gases produces an additional small decrease in friction. In instances of high-velocity friction (*e.g.*, carbon brushes in motors), physical adsorption is tremendously important.³⁰ Here, simple evacuation at room temperature produces friction so high that seizure occurs and mechanical disintegration of the carbon proceeds rapidly; yet a partial pressure of 3 mm. of water vapour (or 300 mm. of oxygen) will reduce this wear to zero. Thus, effective graphite lubrication at high speeds requires a layer of carbon-oxygen complexes (formed from either oxygen or water) to which is attached a physically adsorbed water layer. This physically adsorbed water determines the difference between high- and low-speed lubrication.

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A comprehensive bibliography, keyed to this article, may be obtained from the Reviewer on request.

²⁹ Goodman and Rowe, "Chemisorption, Proceedings of the Symposium held at Keele", 1956, Butterworths, 1957, p. 272.

³⁰ Savage, *J. Appl. Physics*, 1948, 19, 1.