265. *The Nature of the Solid Carbon–Oxygen Complex. Part I. The Oxidative Action of Graphitic Oxide and Active Carbon plus Oxygen on some Aromatic Amines.*

By A. H. Carter, L. de V. Moulds, and H. L. Riley.

Carbon and oxygen can be associated in the solid phase in (*a*) graphitic oxide, (*b*) the substance formed when active carbon combines with oxygen, and (*c*) C_xO_y, the intermediate oxide formed during carbon combustion, the existence of which was originally suggested by Rhead and Wheeler (J., 1912, **101**, 846; 1913, **103**, 461). The following facts suggest that there are close chemical and physical similarities between these three substances. (*a*) On thermal decomposition, graphitic oxide yields carbon monoxide and dioxide, but no free oxygen. Berthelot and Petit (*Compt. rend.*, 1890, **110**, 101) obtained a $CO : CO_2$ ratio of 3 : 2 in the thermal decomposition of graphitic oxide prepared from kish. Kohlschütter and Haenni (*Z. anorg. Chem.*, 1919, **105**, 121) reported $CO : CO_2$ ratios of 1·54—2·04, according to the method of decomposition. (*b*) Only a very small part of the oxygen adsorbed by active charcoal can be removed by evaporation at ordinary temperatures. On raising the temperature it is evolved as oxides of carbon. (*c*) The balance of evidence appears to be in favour of the view that carbon monoxide and dioxide are formed simultaneously in the primary reaction during the combustion of carbon (Riley, *J. Inst. Fuel*, 1937, **10**, 149). (*d*) The metallic electrons of the graphite crystal lattice are concerned in the bonding of the oxygen in graphitic oxide, for Hofmann and his co-workers (*Annalen*, 1934, **510**, 1) have shown that the latter is a non-conductor of electricity. (*e*) Siebel (*Z. Physik*, 1931, **4**, 288) found that the electrical resistance of carbon is slightly increased by simple exposure to air, suggesting that here again the metallic electrons are concerned in the adsorption of oxygen. (*f*) Meyer (*Z. physikal. Chem.*, 1932, *B*, **17**, 385) has shown that when a graphite filament adsorbs oxygen at high temperatures its electrical conductivity decreases. (*g*) The temperature at which graphitic oxide decomposes rapidly depends upon the method of heating. Kohlschütter and Haenni (*loc. cit.*) obtained decomposition ("verpuffen") temperatures varying from 134° to 193° according to the rapidity of the heating. (*h*) Berl and Weingärtner (*Z. physikal. Chem.*, 1932, *A*, **161**, 315) reported an ignition temperature as low as 215° for a sample of activated beechwood charcoal, *i.e.*, one free from appreciable amounts of volatile matter. (*i*) Hofmann and co-workers (*loc. cit.*) have shown by means of *X*-rays that the oxygen atoms in graphitic oxide are bonded between the layer planes of the graphite crystal lattice (see also Balfour, Riley, and Robinson, J., 1936, 456). (*j*) The concept of the mesomorphous state of active carbons (Berl, Andress, Reinhardt, and Herbert, *Z. physikal. Chem.*, 1932, *A*, **158**, 273; Berl and Reinhardt, *ibid.*, 1933, *A*, **166**, 81) and the fact that in very small graphite crystallites the hexagon planes become further apart (Randall and Rooksby, *Nature*, 1932, **129**, 280) indicate that the hexagon-plane surfaces in active carbons may be accessible to molecular oxygen at ordinary temperatures. (*k*) Boersch and Meyer (*Z. physikal. Chem.*, 1935, *B*, **29**, 59) have shown by means of electron rays that the graphite crystal lattice expands, concertina-like, along the *C*-axis when it is exposed to oxygen at high temperatures (700—950°) (see also Eucken, *Z. angew. Chem.*, 1930, **43**, 986).

Lowry and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1408) suggested that a solid surface oxide of carbon, perhaps similar to Brodie's graphitic oxide, plays an important intermediate part in the combustion of carbon.

The above considerations led us to undertake the following experiments with a view to learn something of the chemical nature of the oxygen present in graphitic oxide. Any knowledge gained in this direction has an important bearing upon the complex problems associated with the combustion of carbon. Preliminary experiments indicated that a study of the oxidative action of graphitic oxide on aniline and mono- and di-methylanilines would yield interesting results. The procedure adopted was simple: excess of the amine was warmed with graphitic oxide on the water-bath under reflux until the reduction of the oxide was more or less complete. The following products were obtained: (a) *From pure aniline*: azophenine (2 : 5-dianilino-*p*-benzoquinonedianil), and a dye of the mauveine type. (b) *From commercial aniline* (containing *o*- and *p*-toluidine): a rosaniline dye, in addition to the above products. (c) *From methylaniline*: *NN'N''*-trimethylrosaniline, probably containing some less highly methylated homologues, and a complex uncrystallisable resinous material, which on distillation gave a complex uncrystallisable viscous oil. (d) *From dimethylaniline*: methyl-violet (as sulphate), leuco-crystal-violet (4 : 4' : 4''-trisdimethylaminotriphenylmethane) and 4 : 4'-bisdimethylaminodiphenylmethane. The triphenylmethane dyes produced in these oxidations were sulphates, the sulphate ion being provided by the sulphuric acid occluded in the graphitic oxide. The formation of azophenine in the oxidation of pure aniline indicated that the methane carbon atom in the phenylmethane compounds produced in the other experiments was not derived from the graphitic oxide but probably from the methyl group in *p*-toluidine in the case of the rosaniline, and from one of the amine methyl groups in the case of the other compounds. This view is supported by the observation of E. and O. Fischer (*Ber.*, 1878, **11**, 2099) that dimethylaniline heated with lead dioxide in dilute sulphuric acid solution at 30—40° gave formaldehyde and crystal-violet.

The formation of azophenine in the oxidation of aniline and of the di- and tri-phenylmethane bases in the oxidation of dimethylaniline shows that the amine hydrogen atoms play an important part in the reaction. The formation of highly complex products from monomethylaniline can perhaps be explained by the possibility of the occurrence in this case of both the azophenine type and the hydrocarbon base type of reaction. Von Braun (*Ber.*, 1908, **41**, 2147) has described the preparation of 4 : 4′-bismethylaminodiphenylmethane by condensing methylaniline with formaldehyde, and it is of interest that in this reaction a considerable amount of complex resinous material was formed.

An attempt was made to calculate an oxygen balance in these reactions. This was difficult, for the exact mechanisms of the reactions involved were not known. In the case of aniline the yields of azophenine and pseudo-mauveine-type of compound accounted for approximately 40% of the active oxygen present in the graphitic oxide as estimated volumetrically by means of ferrous sulphate. In the dimethylaniline oxidation the yields of methyl-violet, leuco-crystal-violet and 4 : 4′-bisdimethylaminotriphenylmethane accounted for approximately 30% of the active oxygen. No estimate could be made of the oxygen remaining in the residual carbon : the presence of some was shown by the fact that the carbon on being dried and heated decrepitated slightly.

When aniline is oxidised by the reagents mentioned, the following products are obtained : hydrogen peroxide or sodium peroxide in dilute acetic acid, 2 : 5-dianilinobenzoquinonemonoanil (Schunk and Marchlewski, *Ber.*, 1892, **25**, 3574) : sodium peroxide and stronger acids, aniline-black (Fischer and Trost, *ibid.*, 1893, **26**, 3083) ; hydrogen peroxide in neutral solution, benzene, azobenzene, and a little nitrobenzene (Bamberger and Tschirner, *ibid.*, 1898, **31**, 1523) ; neutral persulphate, 2 : 5-dianilinobenzoquinonemonoimide (Caro, *Z. angew. Chem.*, 1898, **11**, 848 ; Willstätter and Majima, *Ber.*, 1910, **43**, 2590) ; ammonium persulphate, aniline-black (Börnstein, *Ber.*, 1901, **34**, 1286 ; Willstätter and Dorogi, *ibid.*, 1909, **42**, 4126) ; permonosulphuric acid, nitrobenzene and phenylhydroxylamine (Bamberger and Tschirner, *ibid.*, 1899, **32**, 1675) ; lead dioxide on aniline vapour, phenazine (Schichutzki, *ibid.*, 1874, **7**, 1454) ; lead dioxide on a neutral aniline solution at 100°, 2 : 5-dianilino-*p*-benzoquinoneimidanil, azophenine, and a little azobenzene (Börnstein, *loc. cit.* ; Majima and Aoki, *Ber.*, 1911, **44**, 3080 ; Goldschmidt, *ibid.*, 1920, **53**, 34 ; Goldschmidt and Wurzschmitt, *ibid.*, 1922, **55**, 3221) ; lead dioxide in sulphuric acid, quinone and intermediates in aniline-black formation (Willstätter and Dorogi, *ibid.*, 1909, **42**, 2155).

Peroxides and lead dioxide in very weakly acid or neutral solutions thus oxidise aniline to iminoquinone derivatives. The fully condensed azophenine is only obtained in quantity by the use of lead dioxide. The above experiments thus indicate that graphitic oxide is similar in its action as an oxidising agent to lead dioxide and to hydrogen peroxide, and it can be concluded that the oxygen in graphitic oxide is present at a potential similar to that of the oxygen in these compounds.

The formation of leuco-crystal-violet and 4 : 4′-bisdimethylaminodiphenylmethane in the oxidation of dimethylaniline is somewhat surprising, particularly when methyl-violet is simultaneously produced. The formation of the latter is intimately connected with the presence of occluded sulphuric acid in the graphitic oxide (see below). Careful examination of the reaction product failed to reveal the presence of the carbinol base. Hitherto, leuco-crystal-violet has been prepared by various condensation reactions, *e.g.*, that of dimethylaniline with orthoformic ester (Fischer and Körner, *ibid.*, 1884, **17**, 99) or with dichloroguanidine (Gatterman and Schnitzpahn, *ibid.*, 1898, **31**, 1774) ; or by the action of various reducing agents on the crystal-violet carbinol base, *e.g.*, tin and hydrochloric acid (Wichelhaus, *ibid.*, 1881, **14**, 1952 ; 1883, **16**, 2007), followed by alkali. Similarly, 4 : 4′-bisdimethylaminodiphenylmethane may be prepared by the reduction of Michler's ketone (Nathansohn and Müller, *ibid.*, 1889, **22**, 1882) or by various condensation reactions with dimethylaniline (Cohn, *Chem.-Ztg.*, 1900, **24**, 564 ; Doebner, *Ber.*, 1879, **12**, 812 ; Hanimann, *ibid.*, 1877, **10**, 1235). Neither has hitherto been produced by a direct oxidation such as that with graphitic oxide.

Both these bases, in the cold in dilute acid solution, are immediately oxidised to the brightly coloured salts of their respective carbinol bases on the addition of a little lead or manganese dioxide. The addition of graphitic oxide to the dilute acid solution did not give the coloured salt, even on prolonged boiling. It is perhaps significant that hydrogen peroxide also does not convert the hydrocarbon bases into the coloured carbinol salts, even when boiled with them in acid solution. This may be a solvent effect, as the oxidising properties of graphitic oxide are not so marked in presence of excess of water. This result, however, appears to offer some experimental support for the suggestion (Balfour, Riley, and Robinson, *loc. cit.*; cf. Hofmann, Frenzel, and Csalán, *loc. cit.*) that the oxygen in graphitic oxide is peroxidic in character, although perhaps it is not legitimate to compare the behaviour of aqueous hydrogen peroxide with the oxidative activity of a solid complex like graphitic oxide.

The above experiments indicate that, in certain cases, graphitic oxide might prove a useful oxidising agent. The temperature at which it will act depends upon the nature of the substance oxidised. Heated alone, it commences to decompose at temperatures as low as 130—140°. The carbon formed in its decomposition is decidedly active (Lowry and Morgan, *J. Physical Chem.*, 1925, **29**, 1105). This might be advantageous in certain circumstances.

A series of parallel experiments, employing air in the presence of active charcoal as the oxidising agent, were also carried out. A few grams of active charcoal granules were added to the amine, and air was bubbled through the mixture for several hours whilst it was heated on the water-bath. The most striking results were obtained with the methylanilines. Dimethylaniline gave leuco-crystal-violet and 4 : 4'-bisdimethylaminodiphenylmethane. When the active charcoal was previously treated with dilute sulphuric acid, or if a little acid was added to the amine, methyl-violet was also produced. Monomethylaniline gave a complex uncrystallisable resin, similar to that obtained with the graphitic oxide. When an acid-treated charcoal was used, the triphenylmethane dye was also obtained. This striking parallelism between the oxidative activity of graphitic oxide and of oxygen in the presence of active carbon can leave little doubt as to the fundamental similarity between graphitic oxide and the active carbon–oxygen complex. It is noteworthy in this connection that Kade and Ignatjew (Russ. P. 23917, 13/10/1931) observed the formation of methyl-violet when hot air was passed through a solution of dimethylaniline and phenol in the presence of activated wood charcoal and sodium chloride.

The parallelism in the case of aniline is not quite so close. With active charcoal (both acid and neutral) and oxygen, tarry products were formed at 100°, from which only small quantities of impure crystalline products could be isolated. These could not be definitely identified, but their colour reactions with concentrated sulphuric acid indicated that they were iminoquinone derivatives. On using a sulphuric acid-treated charcoal at the b. p. of aniline, a small amount of azophenine and a few grams of some substance, probably closely allied to induline-3B, were formed. Some rosaniline was also formed when an acid-treated active carbon was employed with a synthetic mixture of aniline and *o*- and *p*-toluidine.

This difference in the behaviour of graphitic oxide and oxygen + active carbon is due perhaps to some subtle difference in these substances, or perhaps to the fact that aniline is oxidised to tarry products at an appreciable velocity by oxygen alone. The above experiments, together with the work of Hofmann *et al.* (*loc. cit.*) on the structure of graphitic oxide and of Berl *et al.* (*loc. cit.*) on active carbons, offer convincing evidence that when carbon reacts with or adsorbs oxygen the latter may, in certain circumstances, penetrate between the hexagon layer planes of the graphite crystallites.

EXPERIMENTAL.

Preparation of Graphitic Oxide.—Finely divided Ceylon graphite (10 g.) was added to a mixture of concentrated sulphuric acid (300 c.c.) and concentrated nitric acid (150 c.c.; *d* 1·4) in a litre bolt-head flask. The mixture was stirred automatically, and potassium chlorate (200 g.) added in small portions during 4—6 hours. Chlorine dioxide was prevented from accumulating over the liquid, and exploding, by drawing a rapid current of air through the flask by means of a tube, one end of which was placed just above the surface of the reaction mixture and the other end connected to a filter-pump. After the addition of the chlorate, the reaction mixture was poured into 2 l. of water, the green product, which still contained some unchanged carbon, was washed three times by decantation, filtered off, pressed as dry as possible, and again treated with the concentrated acids and potassium chlorate. After 2—3 hours' stirring it was left overnight. The pale green glistening leaflets so produced were washed four times by decantation with tap water, which removed solid potassium chlorate, chloride, etc., and then 6—8 times with distilled water. The supernatant liquid then contained a fairly stable dispersion of graphitic oxide which would not settle completely within a week. Experience showed that further washing peptised the whole mass, and it was therefore filtered off at this stage and pressed as dry as possible. It was then shaken with and filtered from about 1 l. of dry alcohol thrice, and dried at 60° in an air-oven. During washing, the graphitic oxide became light yellow and then darkened somewhat. The product was light brown. It contained about 10% of available oxygen, as estimated by ferrous sulphate, and small amounts of adsorbed sulphate and chloride. A repetition of the above chlorate treatment would probably have increased the available oxygen, but owing to the pronounced hydrophilic nature of the substance, it was found expedient to oxidise it only twice.

Oxidation of Aniline.—" AnalaR " Aniline (250 c.c.) was heated in a conical flask under a reflux condenser with graphitic oxide (50 g.) for 20 hours on the water-bath. The graphitic oxide was then almost completely reduced, for a little of it deflagrated only slightly on being heated in the Bunsen flame. The reaction product was thoroughly extracted in a large Soxhlet apparatus with 2 l. of benzene followed by rectified spirit. The benzene was removed from the first extract by distillation, and excess of aniline recovered by distillation under reduced pressure, or by steam-distillation. A tarry solid remained, which all dissolved on warming in 500 c.c. of benzene, and the solution on standing deposited reddish-brown crystals which, on recrystallisation from benzene and light petroleum alternately, yielded brick-red crystals of azophenine (2 : 5-dianilino-*p*-benzoquinonedianil), m. p. 246—247°. Further crops of these crystals were obtained from the mother-liquors; total yield 7·1 g. (Found : C, 81·8; H, 5·6; N, 13·1. Calc. : C, 81·8; H, 5·5; N, 12·8%). In hydrochloric acid suspension the crystals became violet, and a characteristic violet solution was obtained in concentrated sulphuric acid, which on dilution became blue and developed a carmine fluorescence (Witt and Thomas, J., 1883, **43**, 115). Exhaustive examination of the benzene-soluble fraction showed that no appreciable quantity of any other compound was present, apart from small amounts of tar and some acetone-soluble material.

The rectified spirit extract on concentration deposited 2·8 g. of a dark blue solid, insoluble in the commoner organic solvents except alcohol. It was slightly soluble in water and gave purple solutions. With sulphuric acid it gave in the cold a dirty olive-green solution, which became blue on slight dilution and purple on further dilution, indicating that the substance was probably pseudo-mauveine or a closely allied compound (Fischer and Hepp, *Annalen*, **1893**, **273**, 315). Owing to the presence of tarry impurities, and possibly also of the sulphate ion, this compound could not be purified by recrystallisation. Some aniline-black was possibly left in the residual carbon.

When ordinary commercial aniline (containing *o*- and *p*-toluidine) was used, the alcoholic extract was much redder, and on evaporation a red, tarry oil was obtained which, when boiled with water, gave a bright red solution which dyed wool directly, the colour being fast to water. On the addition of hydrochloric acid, the solution became pale yellowish-green, and the original colour was restored on neutralisation. Excess of caustic alkali destroyed the colour, rapidly on warming slightly, a white precipitate being formed. The colour was again restored on neutralisation. The bright red solution was bleached rapidly by zinc and hydrochloric acid, and the colour was not restored in air. From these reactions and by analogy with the behaviour of graphitic oxide with the other amines studied, it was concluded that the bright red colour was due to the presence of pararosaniline and closely allied dyes. The acid necessary for the formation of these dyes was provided by the sulphuric acid occluded in the graphitic oxide. When, instead of aniline, a synthetic mixture of aniline and *p*-toluidine was used, on oxidation a red colour developed in a few minutes in a manner similar to that in which methyl- and dimethyl-aniline developed purple and violet colours respectively.

Oxidation of Dimethylaniline.—The dimethylaniline was freed from methylaniline by treatment with acetic anhydride and distillation, the fraction, b. p. 191—193°, being collected. It was treated with graphitic oxide exactly as above but for only 15 hours. The product, which had become intensely violet, was extracted with light petroleum (1½ l.) (Soxhlet), and then by a similar amount of rectified spirit. The brown light petroleum extract was freed from solvent by distillation, and from excess of amine by distillation under reduced pressure. The tarry residue crystallised on standing for 2 days. The crystals were washed with a little ether, becoming white with a bluish-green tinge. The total yield was 21 g. The crystals were soluble in most organic solvents. Repeated recrystallisation from alcohol raised the m. p. from 85°

to 172—174°, the mother-liquors becoming pink in the process. As recrystallisation proceeded, it became obvious that two substances were present, and their separation was effected by slow crystallisation from light petroleum, white needles (1—2 mm. long) and clusters of pale yellow prisms (1 cm. long) being formed. These were separated by hand picking and purified by further recrystallisation from alcohol and light petroleum. From alcohol, the needles formed nacreous plates, m. p. 176°, of leuco-crystal-violet (4 : 4′ : 4″-trisdimethylaminotriphenylmethane) (Found : C, 80·6; H, 8·5; N, 11·4. Calc. : C, 80·4; H, 8·3; N, 11·3%). With methyl iodide in methyl-alcoholic solution it gave a methiodide, m. p. 187—188°. A light petroleum solution of the hydrocarbon base was poured on filter-paper, and on evaporation and exposure to air the paper developed an intense violet colour. This reaction was accelerated by exposure to light.

The long prisms had m. p. 91—92°, undepressed on admixture with authentic 4 : 4′-bisdimethylaminodiphenylmethane (Found : C, 80·6; H, 8·8; N, 11·2. Calc. : C, 80·3; H, 8·7; N, 11·0%). The final yields of the pure products were : leuco-crystal-violet 8 g. ; 4 : 4′-bisdimethylaminodiphenylmethane 7 g.

The deep violet alcoholic extract of the reaction mixture was evaporated to dryness, and the residue recrystallised from water. A further crop of crystals was salted out from the mother-liquors, in all 4·3 g. being obtained. The crystals had the characteristic green sheen and all the other properties of a triphenylmethane dyestuff. The dye was substantive to wool, the dyed wool being stripped by a solution of hydrochloric acid in boiling dilute alcohol. The substance contained a sulphate ion. The above and several other tests left little doubt that the product was methyl-violet in the form of its sulphate. It was somewhat less soluble than commercial crystal-violet, which is a chloride. The source of the sulphate ion was the sulphuric acid adsorbed by the graphitic oxide. It was possible that the substance isolated contained a small amount of incompletely methylated analogues.

No other compound could be isolated from the alcoholic extract, or on further extraction of the residual carbon with various solvents.

Oxidation of Methylaniline.—The reaction was carried out as for the dimethyl-base. The reaction mixture, which had become deep purple, was thoroughly extracted (Soxhlet) with light petroleum, followed by alcohol. The first extract was deep brown, and the second deep purple. The latter was evaporated to dryness, the residue washed with ether to remove tarry products and then recrystallised from water, crystals (3·1 g.) with a green lustre, very similar to crystal-violet, being obtained. Its reactions showed it to be a triphenylmethane dye, and by analogy with crystal-violet it was concluded that it was *NN′N″*-trimethylpararosaniline, which probably contained a small amount of less highly methylated analogues. It dyed wool with a shade intermediate between those of crystal-violet and of rosaniline.

The light petroleum extract was worked up as for dimethylaniline. A strong smell of carbylamine was noticed. (Excess of methylaniline was also removed by steam distillation.) The residue in the flask (about 30 c.c.) on cooling set to a hard, brown, vitreous, resin-like mass. Attempts to crystallise this from various solvents gave only flocculent, dark brown precipitates. The resin was therefore distilled at 1 mm. pressure. A turbid orange-coloured oil commenced to distil at 90°, and this became darker and more viscous as distillation proceeded. Nothing further distilled above 260°. Redistillation gave no constant-boiling or crystalline fraction. Attempts to prepare a picrate, methiodide, benzoyl derivative, ferric chloride compound, and nitroso-compound all failed. It was thus concluded that in addition to the triphenylmethane dye, the product of oxidising methylaniline with graphitic oxide was a complex resinous material.

Preparation of Active Charcoal.—The charcoal (quality 75; NL 13) was provided by Messrs. Sutcliffe, Speakman & Co., to whom the authors express their thanks. It was reactivated as follows in order that the graphitic crystallites should be reduced to very small dimensions. The charcoal, contained in a porcelain boat, was heated at 900° in a large silica tube furnace in a stream of dry carbon dioxide, and the degree of activation expressed as a percentage loss in weight. For some of the experiments the activated charcoal was soaked in dilute sulphuric acid for 2 days, drained, and dried at 100°.

Oxidation of Aniline.—Activated (22·5%) charcoal granules were packed in a vertical tube surrounded by an electric furnace and connected at the lower end to a 200-c.c. bolt-head flask and at the upper end to a reflux condenser. Aniline (100 c.c. " AnalaR ") was placed in the flask and heated to boiling, and a slow stream of oxygen bubbled through it. The charcoal was kept at 100° by means of the electric furnace. The aniline turned black, and there was a strong odour of carbylamine in the initial stages. After 8 hours, the dark viscous product was filtered and distilled in a vacuum. The residual charcoal was extracted with benzene, and the extract freed from solvent by evaporation. The residues were principally uncrystallisable tars but small amounts of two substances, probably of the mauveine and azophenine type, were isolated. They were too small for purification and identification, but gave characteristic colour reactions.

Aniline (100 c.c. " AnalaR ") was boiled under a reflux with activated (40%), acid-treated carbon granules (10 g.) whilst a slow stream of oxygen was bubbled through the liquid. After 40 hours, excess of aniline was removed by steam-distillation, and the residue was extracted (Soxhlet) first with benzene and then with alcohol. From the benzene extract, 2 g. of a dark brown tarry solid were obtained which, on repeated recrystallisation from benzene, yielded a small amount of impure azophenine, m. p. 235°, mixed m. p. 241°. It gave the characteristic colour reaction with concentrated sulphuric acid. A tarry, bluish-brown solid was obtained from the benzene mother-liquors. Although it was not possible to purify this substance completely, its solubility in various solvents and its colour reaction with concentrated sulphuric acid (Fischer and Heiler, *Ber.*, 1893, **26**, 384) indicated it to be a compound of the induline type.

The alcoholic extract was deep violet, and on cooling deposited 3 g. of a dark blue powder. This was insoluble in toluene, light petroleum, and cold benzene, slightly soluble in boiling benzene, giving a pale pinkish solution, soluble in alcohol, acetone, and methyl alcohol, giving bluish-violet solutions. It dissolved in aniline, giving a violet solution, and in concentrated sulphuric acid, giving a blue colour. A piece of wool dipped into the alcoholic solution was dyed blue. On immersion in sulphuric acid, the fibre became almost colourless and the solution blue. The compound contained sulphate ion. The free base, liberated by adding caustic soda to the hot alcoholic solution, was obtained as a dark blue flocculent precipitate, which on recrystallising from benzene gave minute crystals with a faint metallic lustre. They softened at 245° but did not melt below 300° (Kehrmann, *Ber.*, 1923, **56**, 2936). These results indicated that at the higher temperature employed condensation had proceeded further than in the other aniline oxidations and that the blue product was probably a mixture of sulphates of compounds of the induline type.

Oxidation of Aniline containing o- *and* p-*Toluidine.*—Acid-treated, activated (40%) charcoal (9 g.) was added to a mixture of aniline (40 c.c.), *o*-toluidine (30 c.c.) and *p*-toluidine (12 c.c.). The mixture was heated under reflux on a water-bath for 40 hours whilst a current of air was bubbled through it. The charcoal was filtered off and extracted with benzene (Soxhlet), giving a reddish-brown solution. The solvent was distilled off, and the residual liquid added to the original filtrate. Excess of amines was removed by steam-distillation, and a brown tar and a red aqueous solution remained. The red solution gave all the characteristic reactions of a rosaniline, and the tar probably contained compounds of the azophenine type, but these could not be isolated in the pure state.

The charcoal was further extracted with alcohol, and a deep reddish-purple solution was obtained which deposited amine sulphates on cooling. Qualitative reactions showed that the solution probably contained a rosaniline dye and a compound of the mauveine type, although it was not possible to isolate sufficient of these substances in the pure state for definite identification.

Oxidation of Dimethylaniline.—Purified dimethylaniline (100 c.c.) was oxidised by gaseous oxygen in the presence of acid-treated, activated (40%) charcoal (50 g.) in the apparatus employing the electric furnace described above. A vigorous reaction occurred, and the amine rapidly darkened. After ½ hour the apparatus was allowed to cool in a stream of oxygen. After several minutes' cooling, a violent explosion occurred which shattered the reaction flask. Subsequent experiments were therefore carried out with air below 100°.

Activated (40%) charcoal granules (20 g.) were placed in a flask fitted with a reflux condenser, and dimethylaniline (100 c.c.) added. A slow current of air was bubbled through the reaction mixture for 20 hours whilst the flask was heated on the water-bath. Excess of amine was then removed by distillation under reduced pressure, and the solid residue recrystallised from light petroleum. The product obviously contained two sets of crystals, which were separated by hand picking. After further recrystallisation from light petroleum, two pure fractions were obtained. One (0·9 g.) consisted of pale yellowish prisms of 4 : 4′-bisdimethylaminodiphenylmethane, m. p. and mixed m. p. 90—91°, and the other (0·35 g.) of white needles of leuco-crystal-violet, m. p. and mixed m. p. 175—176°.

The experiment was repeated with dimethylaniline (100 c.c.) and activated (40%), acid-treated charcoal (20 g.). The air oxidation was continued for 40 hours. The resulting deep violet liquid was filtered, and excess dimethylaniline distilled off under reduced pressure. The residual liquid together with the carbon were extracted with light petroleum, and the resulting brown solution on evaporation yielded 0·6 g. of a crude mixture of leuco-crystal-violet and 4 : 4′-bisdimethylaminodiphenylmethane. The residual carbon was further extracted with methylated spirit, and 7·3 g. of crude methyl-violet were isolated from the solution. This was purified by recrystallisation from water.

A further oxidation, in which sulphuric acid was added directly to excess of amine instead of to the charcoal, gave methyl-violet as the principal product.

Oxidation of Methylaniline.—Methylaniline (100 c.c.) was oxidised by air in the presence of activated (40%) carbon granules (20 g.) at 100° for 40 hours in the manner described above. Excess methylaniline was removed by distillation, and the residual carbon extracted first by light petroleum and then by alcohol. The first extract yielded an uncrystallisable oil similar to that obtained in the graphitic oxide oxidation, and the alcoholic extract yielded no appreciable quantity of any product. The experiment was repeated, sulphuric acid-treated charcoal being used. The liquid became very viscous and dark reddish-purple. After removal of excess methylaniline by distillation under reduced pressure, the residue and charcoal were first extracted with light petroleum, a dark brown uncrystallisable liquid being obtained, and then with alcohol, which gave a deep purple solution from which a purple solid, probably impure *NN'N''*-trimethylpararosaniline sulphate, was obtained.

The authors are indebted to the Research Council of the British Iron and Steel Federation for a grant.

Armstrong College (University of Durham),
Newcastle upon Tyne, 2.

[*Received, May 5th,* 1937.]