Paracyanogen : Its Formation and Properties. Part I.

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The brown residue, obtained by heating oxamide for several hours in a sealed tube, has been shown to be paracyanogen. The chemical and physical properties and infra-red spectra have been compared with those of paracyanogen prepared by thermal decomposition of mercuric and silver cyanides. Some suggestions are put forward with regard to its structure.

In an attempt to grow large crystals of oxamide by slow sublimation a brown residue was found in the hot section of the sublimation tube. It was suspected that this was paracyanogen. The substance was therefore compared with paracyanogen from other sources. These compounds are little known and their structures are undetermined.

Paracyanogen was first noticed by Guy Lussac (*Annalen*, 1816, **53**, 139) during his experiments on heating mercuric cyanide, which led to the discovery of cyanogen. He considered the material to be mainly carbon with a small nitrogen content. Johnston (Brewster's *Edinburgh J. Sci.*, New Series, 1829, **1**; *Trans. Roy. Soc. Edinburgh*, 1840, **14**, 30) reported most of the known properties of paracyanogen. Paracyanogen is most easily prepared from mercury cyanide, and Troost and Hautefeuille (*Compt. rend.*, 1868, **66**, 738) found the optimum conditions were to heat the salt for two days at 440°. It may also be prepared by heating silver cyanide (Redtenbacher and Liebig, *Annalen*, 1844, **50**, 357), silver cyanate (Johnston, *loc. cit.*), cyanogen iodide (Klason, *Ber.*, 1866, **18**, 496), or cyanuric iodide (Bowden and Williams, *Proc. Roy. Soc.*, 1951, *A*, **208**, 176). Paracyanogen has been made by thermal polymerisation of cyanogen under various conditions by Briner and Wroczynski (*Compt. rend.*, 1910, **151**, 314), Perret and Krawczynski (*Bull. Soc. chim.*, 1932, **51**, 622), Jerwen (*Z. physikal. Chem.*, 1916, **91**, 494), and Berthelot and Gaudechon (*Compt. rend.*, 1910, **150**, 1171). Photopolymerisation of cyanogen has been reported (Hogness and Lin-sheng Ts'ai, *J. Amer. Chem. Soc.*, 1932, **54**, 123), as has polymerisation initiated by α-particles (Lind and Bardwell, *Science*, 1925, **62**, 593). Paracyanogen can be produced by electrolysis of potassium cyanide solutions (Hittorf, *Z. physikal. Chem.*, 1892, **10**, 616), by passing hydrogen cyanide or cyanogen into water and igniting the brown precipitate produced (Johnston, *loc cit.*), and by ignition of the precipitate formed when saturated solutions of cyanogen in concentrated aqueous potassium hydroxide or in ether or ethanol (Johnston, *loc. cit.*) are kept. All the investigators found great difficulties in the analysis of their products.

EXPERIMENTAL

Paracyanogen has been found to be formed by a solid-phase polycondensation reaction when oxamide is heated in a sealed glass tube at 250—300°. Oxamide (0·5 g.) in a small sample tube (open at one end) was placed inside a hard-glass tube, 1·2 cm. wide and 10 cm. long, which was then evacuated and sealed with a blow-pipe. Four of these tubes were placed in a steel autoclave together with solid carbon dioxide, 20 g. producing a pressure of about 100 atm. The autoclave was heated in a tubular oven for one week at 270°. After cooling, the glass tubes were opened. The inner sample tubes were heated to 250° for 3 hr. *in vacuo* to remove the residual oxamide by sublimation and also any absorbed water and cyanogen. The conversion was 30—40%. This procedure was adopted for several reasons. The pressure which accumulated in the sealed tube, owing to the vapour pressure of the oxamide and the gaseous products of the reaction, shattered most of the tubes before the compensating autoclave was used. The use of the inner sample tube made the transference of the material from the sealed tube to the high-vacuum apparatus much simpler. Sublimation of the residual oxamide proved an easier method of purification than did washing with hot water. In the final form of the autoclave used, the head, a substantial steel block, was clamped to the body by six high-tensile steel bolts. The contact with the recessed lead washer was made by accurately machined surfaces. The autoclave would withstand a pressure of 130 atm. A Simmerstat of type (TYB) controlled the energy input of the furnace, the temperature remaining within ±1·0°. 25% of the tubes burst; the pressure within the tubes rose continuously so that a satisfactory compensating pressure for a week's heating would be so large that there would be a risk of bursting the tubes in the early stages by too high an excess of pressure. In later experiments only 2 days' heating was given and a 10% yield obtained. The product was dark brown and usually light and porous. Complete polymerisation gave an almost black dense product.

If the inner sample tube was plugged with glass wool, all the product was found inside the inner tube mixed with the oxamide, with only the slightest traces on the walls of the tubes. This shows that the reaction occurs either on the surface of the oxamide or more probably within the crystal by a simple solid-phase condensation. A striking confirmation is given by an electron-microscope photograph (Fig. 1) where the paracyanogen mass is seen growing out of the oxamide crystals.

Preparation of Paracyanogen from Other Sources.—Samples were prepared from mercuric cyanide and from silver cyanide. Either cyanide (5 g.) was placed in a Pyrex tube (1·2 cm. bore, 10 cm. long), which was then evacuated, sealed, and heated for 24 hr. at 440°. After cooling, the tubes were opened by localised heating with a blow-pipe. The silver residues were treated with nitric acid to remove the silver. Then either residue was heated at 300° for 3 hr. *in vacuo* to remove all volatile impurities. Yields were about 80% from mercuric cyanide and 40% from the silver salt. The suffixes (Ox), (Hg), and (Ag) indicate the source of the paracyanogen, *viz.*, oxamide, mercuric cyanide, or silver cyanide.

Analysis of Paracyanogen.—The quantitative analysis of the material proved somewhat difficult owing to its very resistant nature. The normal microchemical methods for the analysis of the carbon and nitrogen proved unsatisfactory. Values of C, 32—34 and N, 32—44% were obtained. Many other methods were tried.

The method finally used was as follows. Paracyanogen (*ca.* 5 mg.) was weighed out on a micro-balance into a Pyrex glass tube of 12 mm. diam. sealed at one end. Potassium sulphate (2 g.), copper sulphate (0·2 g.), and concentrated sulphuric acid were added in such a way that all solid material was washed to the base of the tube. The tube was drawn off, sealed, and heated for 16 hr. at 400°. After cooling, the tubes were opened by cracking, and the acid solution transferred to a standard semi-micro Kjeldahl distillation apparatus, 40% sodium hydroxide being added. The solution was steam-distilled into a saturated boric acid solution (20 c.c.), and and ammonia titrated against N/50-hydrochloric acid with a bromocresol-green–methyl-red indicator. Mean results of four estimations, expressed as percentage of the theoretical nitrogen, were: Paracyanogen (Hg) 96·9%, (Ox) 100·2%.

Chemical Properties.—Paracyanogen is highly resistant to chemical attack. Most of the properties observed by Johnston (*loc. cit.*) have been confirmed. The compound is insoluble in water and most organic liquids. Ignition gives cyanogen or, at much higher temperatures, carbon and nitrogen.

Fusion with potassium gives potassium cyanide, but there is no reaction with fused sulphur or phosphorus. Strong heating in air gives carbon dioxide; in chlorine, cyanogen chloride.

Paracyanogen is soluble in fused potassium hydroxide or in soda-lime to give a deep brown

FIG. 1.

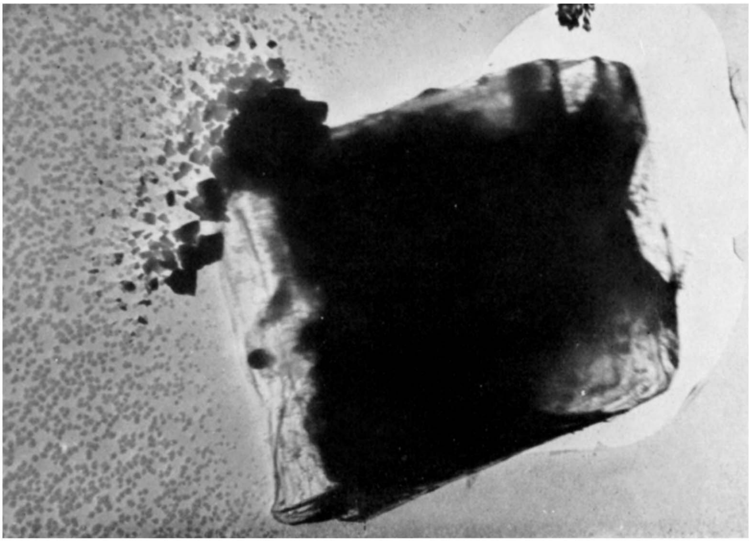
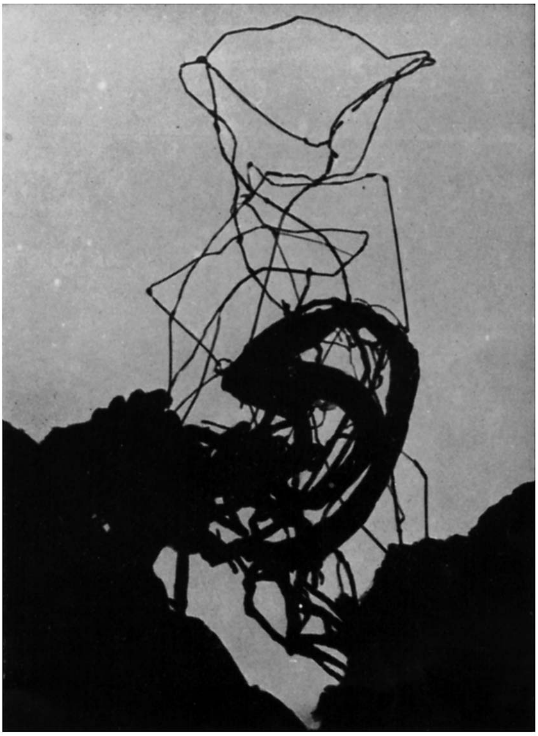


FIG. 3.

FIG. 4.

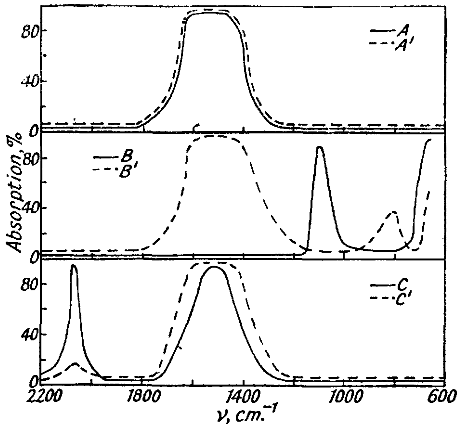


solution which gradually becomes orange-red, then colourless, the solution containing cyanide, cyanate, and carbonate, and ammonia being liberated. It is very slightly soluble in hydrochloric acid but more soluble in concentrated sulphuric acid, from which it is precipitated by water apparently unchanged. The substance is soluble in syrupy phosphoric acid, 60% perchloric acid, and concentrated nitric acid: all these solutions, unlike the solid, exhibit a sky-blue fluorescence in ultra-violet light. The solubility in sulphuric acid is slight, probably less than 1%, although the solution is highly coloured. To make a rough determination of the relative solubilities, a saturated solution in each solvent (2 c.c.) was diluted with water (2 c.c.), and after 24 hr. the relative amounts of precipitate were noted, the sulphuric acid solution being used as a standard. The results for paracyanogen (Ox) were as follows:

Acid used	Colour of solution	Relative wt. of ppt.	Fluorescence
H_2SO_4	Red-brown	10	Sky-blue
H_3PO_4	,,	10	,,
$HClO_4$	,,	8	,,
HNO_3	,,	1	,,
HCl	Faint	Very small	Very faint

Paracyanogen (Ox) dissolved most rapidly in 60% perchloric acid. A much darker solution is given by paracyanogen (Hg) but this is much less easily soluble than paracyanogen (Ox). These sulphuric acid solutions become colourless when heated, cyanogen being evolved.

FIG. 2.



No.	Source and treatment	Absorption frequencies, cm.$^{-1}$	Spectra
1	Paracyanogen (oxamide)	1570 v.s.	*A*
2	,, (mercuric cyanide)	1570 v.s.	*A′*
3	(1) heated to 450° for 24 hr. *in vacuo*	1570 v.s.	as *A*
4	(1) heated to 450° for 16 hr. in air	1100 m., 640 v.s.	*B*
5	(2) heated to 450° for 16 hr. in air	1570 v.s., 810 w., 640 w.	*B′*
6	(1) diss. in conc. H_2SO_4, pptd. by H_2O	2070 v.v.s., 1570 v.s.	*C*
7	(2) diss. in conc. H_2SO_4, pptd. by H_2O	2070 v.w., 1570 v.s.	*C′*
8	(6) heated at 250° for 6 hr. *in vacuo*	2070 w., 1570 v.s.	*C′*
9	(6) heated at 450° for 16 hr. in air	1100 m., 640 v.s.	as *B*
10	(7) heated at 450° for 16 hr. in air	1570 v.s., 810 w., 640 w.	as *B′*
11	Paracyanogen (silver cyanide)	1570 v.s.	as *A′*

Paracyanogen dissolved in fused potassium hydrogen sulphate to give the characteristic deep red-brown solution.

Oxidation Reactions.—If paracyanogen is heated in air at 450° for 16 hr., a brick-red compound of unknown constitution is formed. The normal micro-analysis techniques give variable results for this material. The compounds produced from paracyanogen (Ox) and (Hg) appear to be the same, but their infra-red absorption spectra (Fig. 2) show that they are different. These substances are not produced by similar treatment *in vacuo*, and the amount formed is about 10% by weight of the material used.

The red compound from paracyanogen (Ox), when heated for 1 hr. in a stream of hydrogen, yields a black compound, which on treatment with concentrated sulphuric acid gives a white insoluble substance. The constitution of neither of these compounds is known and neither fluoresces.

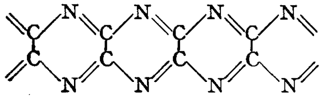
The results obtained by Johnston in the oxidation of paracyanogen by concentrated nitric acid were confirmed. A solution of paracyanogen in concentrated sulphuric acid was added dropwise to boiling nitric acid, giving a pale straw-coloured solution. Addition of mercurous sulphate solution produced a brown flocculent precipitate which gradually formed amber needle-shaped crystals of " mercury paracyanate." Both the acid solution and the mercury derivative gave a sky-blue fluorescence.

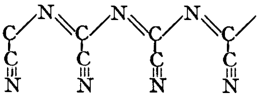
Physical Properties of Paracyanogen.—The paracyanogens and some of their derivatives have been examined by infra-red spectroscopy, and by electron microscopy in an attempt to elucidate their structures.

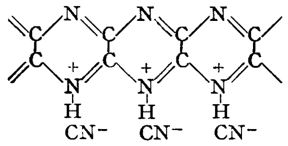
Infra-red absorption spectra. The measurements were made in a Grubb–Parsons spectrometer fitted with a sodium chloride prism. The samples were dispersed in Nujol oil and sandwiched between rock-salt plates. The oil had the twin effects of binding the material and reducing light scatter. The results are shown in the Table and Fig. 2. Some of the bands, especially those at 1570 cm^{-1}, are rather broad and the centres are not very distinct. The intensities given (s. strong, m. medium, w. weak, v.w. very weak) are approximate since it was difficult to keep the absorbing film exactly the same in each case. The numbers in the text refer to the samples in the Table.

The principal paracyanogens, 1, 2, 11, show only the one strong band at 1570 cm.$^{-1}$, which indicates that they have a complete conjugated double-bond system. The spectrum is that which would be expected of a structure such as (I), or particularly the structure with all the C–N bonds equivalent obtained by resonance between this form and that got by interchanging the C–N double and single bonds.

Heating paracyanogen (Ox) *in vacuo* at 450° (3) has no effect. Heating in air at the same temperature (4) has a profound effect, the residue showing no band at 1570 cm.$^{-1}$ but absorption at 1100 and 640 cm.$^{-1}$ instead. Heating paracyanogen (Hg) (5) at 450° in air introduces two weak bands at 810 and 640 cm.$^{-1}$: it is impossible to assign these to any known structural grouping.


(I)


(II)


(III)

Dissolution in sulphuric acid, followed by precipitation in water, also affects the spectra, a new band appearing at 2070 cm.$^{-1}$ which is extremely strong with paracyanogen (Ox) and weak in paracyanogen (Hg). This frequency is too low for absorption by a simple cyanide group (2250 cm.$^{-1}$) or even an *iso*cyanide group (2160 cm.$^{-1}$), though such groups attached to a conjugated system might absorb at lower frequencies. The structure (II) is possible, though a shift of 180 cm.$^{-1}$ on account of conjugation is rather large. Two other cyanide groupings might be considered, adsorbed hydrogen cyanide (gas-state frequency, 2090 cm.$^{-1}$) and cyanide ions (2080 cm.$^{-1}$). The samples were dried in high vacuum so if hydrogen cyanide is present it is tenaciously retained, but salt formation is a possibility (III). The intensity of the 2070 cm.$^{-1}$ band is reduced greatly after 6 hours' heating to 260° *in vacuo* but the band is still detectable in the product.

Heating of the precipitated samples (6) and (7) in air gave rise to products with the same spectrum as the similar products from their parent paracyanogens, *i.e.*, (9) resembles (4) and (10) resembles (5).

To summarise, the paracyanogens are similar in structure though they vary in their resistance to attack. Paracyanogen contains a large conjugated double-bond system and no free cyanide groups, but these might be introduced by treatment with sulphuric acid, possibly owing to some salt formation. Oxidation by air destroys the whole structure.

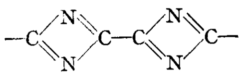
Electron-microscope Photographs.—The various preparations of paracyanogen were examined under an electron miscroscope. At 9000× magnifications paracyanogen (Ox) appeared as a very crumpled torn film, perhaps owing to a preference for growing in the same plane rather than building up in layers. Fig. 1 shows partly converted oxamide at a magnification of 3500. The zone of decompositions can be clearly seen spreading from the corner of the paracyanogen mass into the oxamide crystals. The growth of a large mass of paracyanogen from the minute oxamide crystals is remarkable and must mean that the reaction spreads from one crystal to another.

Paracyanogen (Hg) at 12,000× magnification (Fig. 3) has the appearance of frozen droplets. Watson (*J. Phys. Chem.*, 1947, **51**, 654) noticed that a polymer of hydrogen cyanide, prepared by α-ray bombardment of the gas, when observed under an electron microscope appeared to be an agglomerate of globules. However, paracyanogen (Ag) appeared to be an opaque mass composed of small ill-defined pieces. When an intense beam of electrons was applied to one corner of a large mass a considerable number of fibres unfolded from the mass (Fig. 4, 6500×). The thick inner fibres appeared first. These fibres are similar to those of paracyanogen (Hg).

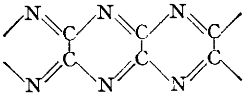
The paracyanogen samples from all three sources, after precipitation from sulphuric acid solution, appeared as shapeless ill-defined masses.

DISCUSSION

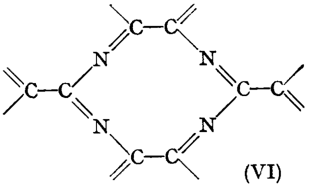
In a solid-phase reaction, such as the formation of paracyanogen from oxamide, those changes which involve least lattice disturbance would be expected to occur most easily. Oxamide has a planar lattice structure (Misch and Van der Wyk, *Compt. rend. Soc. Phys. Hist. Nat. Genève*, 1938, **55**, 97) with very weak inter-planar bonding but very strong intermolecular bonding within the phase. It is possible then that paracyanogen similarly has a planar structure and all the available evidence supports this theory. On this basis three molecular structures can be drawn, *viz.*, (IV)—(VI). These structures are consistent with the results obtained by infra-red spectroscopy, which indicate the presence of a conjugated double-bond system. A 20-membered ring system can also be drawn but will not be considered further.



(IV)



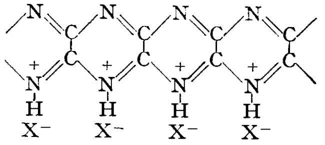
(V)



(VI)

The four-membered ring system (IV) is essentially a linear polymer with free rotation about the C–C bonds. The six-membered ring structure (V) is a " ribbon " polymer, and the ten-membered ring system (VI) an infinite sheet. However, if molecular models are constructed only formula (V) can be made without excessive strain.

In the lattice planes of oxamide the molecules lie in rows linked by hydrogen bonding to form an infinite sheet. From the grouping of molecules in the plane of both the four- and the six-membered ring, structures for paracyanogen could easily be formed by the simple elimination of water across the hydrogen bonds, between adjacent amide groups.



($X^- = HSO_4^-$) (VII)

The fluorescence of the paracyanogen solutions in concentrated mineral acids suggests that a resonating ring structure exists, and that in solution the molecule is ionised, possibly in the form (VII). The solvated multivalent ion is consistent with the intense colouring and the fluorescence of the solutions, and also with the precipitation of paracyanogen on addition of water to the anhydrous acid solutions. Structure (VI) would make paracyanogen unlikely to dissolve; the infinite planar lattice could only accept anions in layers between the planes, forming a colloidal suspension rather than a solution.

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