The Cyanogen Halides. Part II. The Positive Cyanogen Ion.*

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Evidence is presented for the existence of a positive cyanogen ion in solution. Cyanogen chloride forms double halides analogous to nitrosonium salts. Consideration of the energetics of the process indicates that these compounds are unlikely to be salts in the solid state. The enhancement of the conductivity of cyanogen chloride by these compounds and not by chlorides which do not form complexes, shows that they ionize in solution. The mode of ionization follows from the anionic transport of the metal on electrolyses of aluminium and ferric chloride complexes. Cyanogen bromide behaves similarly, although polymerization obscures the results. Aromatic substitution by double halides in Friedel–Crafts reactions, and the reactions of cyanogen halides with organometallic compounds, are in agreement with the existence of a positive cyanogen ion in solution. Attempts to prepare cyanogen fluoride and its complex fluorides are described.

Solvolytic ionization of cyanogen halides was discussed by Fairbrother (*J.*, 1950, 180), who pointed out that the ionization of cyanogen chloride to Cl^- and CN^+ is more favourable than to Cl^+ and CN^- with the consequence that there are few, if any, reactions of cyanogen chloride in which it behaves as a cyanide. It follows that the positive cyanide ion must have a finite existence in solution and may even have a permanent existence in the solid state. This paper provides further evidence for this conclusion.

The analogies between cyanogen halides and nitrosyl and interhalogen halides (cf. Part I *) can be usefully extended to a comparison of the positive ions formed from these substances. Older evidence for the nitrosyl ion has been given by Weiss (*Ann. Reports*, 1947, **44**, 73), and since then the use of proton-free ionizing solvents (sulphur dioxide, nitrosyl chloride, and bromine trifluoride) has provided ample confirmatory evidence (Seel and Bauer, *Z. Naturforsch.*, 1947, **2**, ***b***, 397; Seel, Bocz, and Nogradi, *Z. anorg Chem.*, 1951, **264**, 298; Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1964; Burg and McKenzie, *ibid.*, 1952, **74**, 3143; Woolf, *J.*, 1950, 1053).

The evidence for halogen cations is not so extensive (Reeve, *Rev. Pure Appl. Chem. Australia*, 1952, **2**, 108). It is based mainly on their halogenating ability and salt formation (Derbyshire and Waters, *J.*, 1950, 564, 573; Carlsohn, *Ber.*, 1935, **68**, 2209; Fialkov and Shor, *J. Gen. Chem., U.S.S.R.*, 1949, **19**, 1198; Gutmann, *Z. anorg. Chem.*, 1951, **264**, 152). The important feature of this work is the necessity of solvation to stabilize halogen cations both in solution and in the solid state.

Methods similar to those used for the study of nitrosyl and halogen cations have been applied to show the existence of a positive cyanogen ion. Compound formation between cyanogen chloride and halides was investigated. The chlorides used are listed in Table 1 and will be considered in turn. The 1 : 1 compound with gold chloride was a yellow crystalline solid which formed a red solution in cyanogen chloride. All attempts to prepare the boron compound by evaporation of solutions *in vacuo* led to an exothermic polymerization of cyanogen chloride. The aluminium chloride compound may be partly polymerized, because it had to be prepared at 100°, but the fact that the same compound was produced by rapid heating to 100°, or by slow heating to 100° after being kept for several hours at room temperature. renders this unlikely. The titanium compound was not that obtained

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* Part I, *J.*, 1953, 4121.

by Wohler (*Annalen*, 1850, **73**, 219) whose analysis showed a 1 : 1 compound; when prepared from liquid cyanogen chloride its composition was always $TiCl_4,2CNCl$, and it was a yellow solid, sparingly soluble in cyanogen chloride. The corresponding stannic compound could not be prepared even in liquid sulphur dioxide. Antimony pentachloride was the only halide in Group V which reacted. Compounds with PCl_3, PCl_5, $AsCl_3$–Cl_2 (reported to react as $AsCl_5$; Gutmann, *Monatsh.*, 1951, **82**, 473), and $SbCl_3$ could not be isolated. The ferric chloride compound had not been previously identified although Klein (*loc. cit.*) mentioned the reaction with ferric chloride. It was a brown solid which dissociated at <5 mm. and formed a deep red solution in cyanogen chloride. The corresponding nitrosyl compounds are given in the same Table, and it is significant that all the cyanogen compounds have nitrosyl analogues and that, from their composition at least, the former could be formulated as salts of a positive cyanogen ion. The latter ion should be spherically symmetrical by rotation. The upper limit to its size, 1·40 Å, is fixed by the radius of the nitrosonium ion with two extra orbital electrons. (The use of covalent radii to obtain the upper limit in size is only reliable if the centre of rotation is known. For example, the upper limit to the radius of the nitrosonium ion would be equal to the covalent nitrogen–oxygen distance, 1·15 Å, if it were to rotate about the centre of this bond.) The radius of the positive cyanogen ion should therefore be closer to that of the sodium than of the potassium ion (0·95 and 1·33 Å, respectively). Since the radius ratio decides the structure in ionic lattices, the compound $(CN)_2TiCl_6$ should be isomorphous with the sodium salt. However, *X*-ray powder photography reveals no simple symmetry for the cyanogen compound, whereas the sodium salt is cubic (Engel, *Z. Krist.*, 1935, **90**, 362). A comparison of the energetics of complex salt formation with the cyanogen and nitrosyl positive ions shows that the former is far less favoured. Consider the process

TABLE 1. *Double halides of cyanogen and nitrosyl chlorides.*

Chloride	Compound with : CNCl	Compound with : NOCl[1]	Chloride	Compound with : CNCl	Compound with : NOCl[1]
$AuCl_3$	1 : 1	1 : 1	$TiCl_4$	1 : 2	1 : 2
BCl_3	1 : 1[2]	1 : 1	$SnCl_4$	—	1 : 2
$AlCl_3$	1 : 1	1 : 1	$PbCl_4$	—[3]	1 : 2
$FeCl_3$	1 : 1	1 : 1	$SbCl_5$	1 : 1[4]	1 : 1
$PtCl_4$	—	1 : 2			

$ZrCl_4$,[4] $ThCl_4$,[4] PCl_3, PCl_5, $AsCl_3$, $SbCl_3$, and $NbCl_5$ do not form compounds.

[1] See Seel, *Z. anorg. Chem.*, 1950, **261**, 76, for references. [2] Martien, *Annalen*, 1859, **109**, 74. [3] Matthews, *Amer. Chem. J.*, 1898, **20**, 815. [4] Klein, *Annalen*, 1850, **74**, 87.

$$\begin{aligned} X\text{–}Cl(g) &\longrightarrow X(g) + Cl(g) \longrightarrow X^+(g) + Cl^-(g) \\ Cl^-(g) + MCl_x(g) &\longrightarrow MCl_{(x+1)}^-(g) \\ X^+(g) + MCl_{(x+1)}^-(g) &\longrightarrow XMCl_{(x+1)}^-(s) \end{aligned}$$

where X–Cl is cyanogen or nitrosyl chloride, $MCl_{(x+1)}^-$ the complex anion, and the letters (g) and (s) refer to the gaseous and the solid state. The three terms which differ are the dissociation energy of the X–Cl bond, the ionization energy of the positive ion, and the lattice energy of the salt. Only the last term is more favourable for salt formation from cyanogen chloride, because of the smaller size of the cyanogen positive ion; but this is far outweighed by the difference in dissociation energies (~58 kcal.) and ionization potentials (~67 kcal., if the ionization potential of cyanogen and bromine radical are assumed equal; the direct measurement for the former of 14 ± 2 ev probably includes some extra excitation energy).

The cyanogen compounds may not be ionic in the solid, but experiments using cyanogen chloride as a solvent gave definite evidence for ionization in solution. The conductivity of cyanogen chloride reported in Part I (*loc. cit.*) was considerably enhanced by addition of chlorides with which it formed compounds. A M/50-solution of aluminium chloride, for example, was 1000 times as conducting, and the equivalent conductivity was of the same order as in liquid nitrosyl chloride. In contrast, arsenic trichloride, typical of halides soluble in cyanogen chloride without compound formation, provided a negligible increase.

Values of the equivalent conductivity at infinite dilution obtained by extrapolation of the results with concentrated solution (0·01—0·10M) are given below and are to be regarded as rough minimum values.

Solute	$AlCl_3$	$SbCl_5$	$FeCl_3$	$AsCl_3$
Λ_∞, approx.	82	>18	82	0·2

The increase in conductivity with antimony pentachloride was perhaps the most significant result. The reasons for believing that this is not due to ionization of the pentachloride itself are, first, that the latter is a covalent halide, whose conductivity has been redetermined as 5×10^{-8} mho at room temperatures, and which would hardly be expected to ionize in so weakly an ionizing solvent as cyanogen chloride; and, secondly, that arsenic trichloride, which could ionize more readily, barely increases the conductivity of the solvent. It is therefore difficult to account for the observed increase with the pentachloride, or even with ferric and aluminium chlorides, both of which have layer lattices in the solid state, unless complex formation with the solvent to form a complex anion is assumed.

The analogy with nitrosyl chloride provided an indication of the direction of ionization, but the failure of cyanogen chloride to undergo polyhalide formation prevented a confirmation of this direction by the use of exchange reactions. The solutions were therefore electrolysed with the expectation that metal would be transported to the cathode if the positive cyanogen ion were present in solution.

The compound $CNCl,AlCl_3$ is in equilibrium with ions in solution: $CNCl,AlCl_3 \rightleftharpoons CN^+ + AlCl_4^-$. The anion is also in various equilibria with chloride ions. Whether aluminium is transported to the anode or the cathode depends on the stability of the complex ions, governed by the various equilibrium constants, and the rate of the possible electrode processes governed by their activation energies. (It is reasonable to assume that attainment of ionic equilibria is instantaneous and does not affect the rate of the overall process.) The deposition or transport of metal to the anode, therefore, is acceptable evidence for its presence in an anion, but the reverse process does not necessarily imply that it is originally present as a cation or cation complex. A further complication arises when transport is the main phenomenon, which depends on the relative mobilities of the complex anions and cations in equilibria. If these mobilities are sufficiently different, the net observed movement of the element in a given direction may be the opposite to that expected for ions present in the larger amount. In practice, this may be unimportant because equilibrium constants of complex anions of the type investigated are usually small in most solvents, whereas transport numbers will not differ by more than a factor of 100. Van Dyke (*J. Amer. Chem. Soc.*, 1950, **72**, 3619) maintained that, because electrolysis of aluminium bromide in methyl bromide gave aluminium at the cathode and bromine at the anode, it behaved as a normal 1 : 3 electrolyte. The electrolysis products, however, could result from aluminium bromide in equilibrium with a complex anion and the above experiment does not disprove the presence of $AlBr_4^-$ ions. Wertyporoch (*Ber.*, 1931, **64**, 1378), using ethyl bromide solutions, came to an opposite conclusion, but examination of his results does not support the contention that aluminium migrates to the anode in a complex anion. He calculated the ratio of the anodic to cathodic aluminium in solution at the end of electrolysis, but if the ratio of the losses in concentrations at the electrodes is calculated, an inverse ratio is obtained. It appears that aluminium is primarily deposited at the cathode rather than transported to the anode. Electrolysis of aluminium chloride solution in cyanogen chloride, under anhydrous conditions with platinium electrodes, produced an increase in aluminium concentration above the original at the anode and a decrease at the cathode. With ferric chloride solution the result was not as definite although the anode concentration was greater than the cathode value. When silver electrodes were substituted in a ferric chloride solution, deposition rather than transport resulted. Iron and paracyanogen were deposited, and cyanogen gas liberated at the cathode, chlorine at the anode. A qualitative electrolysis of an antimony pentachloride solution with a platinium cathode and silver anode showed that paracyanogen and chlorine were formed at anode and cathode, respectively. These experiments concord with an ionization to positive cyanogen in cyanogen chloride solutions; their complete interpretation, however, would require a more complete knowledge of the various equilibria existing in solution, as well as of the relative mobilities of the ions.

Cyanogen bromide behaved similarly to cyanogen chloride, but the easier polymerization to the trimer was a complication. Oberhauser (*Ber.*, 1927, **60**, 1434; 1929, **62**, 1482) prepared some double halides by heating bromides with cyanogen bromide in sealed tubes and extracting the residue with carbon disulphide, or by mixing solutions in organic solvents. He obtained $2CNBr,SnBr_4$, $2CNBr,TiBr_4$, $2CNBr,AsBr_3$, and $3CNBr,2SbBr_3$ by these methods but was unable to prepare any compound with aluminium bromide because of polymerization. In fact, the addition of aluminium bromide to cyanogen bromide is the best method of preparing cyanuric bromide (Perret and Perrot, *Bull. Soc. chim.*, 1940, **7**, 743). The compound $CNBr,AlBr_3$, however, was readily obtained by mixing solutions of the component halides in non-polar solvents. The fact that the composition of the product was independent of the relative proportions of the halides used, showed that polymerisation had not occurred. The conductivity of molten cyanogen bromide was increased immediately on addition of aluminium or stannic bromides but the polymerization of the solvent prevented precise measurement of conductivity or of ionic mobility.

It was expected that complex fluorides of the positive cyanogen ion would be thermodynamically the most stable of complex halides and, consequently, the preparation of double fluorides with cyanogen fluoride was attempted. Cosslett (*Z. anorg. Chem.*, 1931, **201**, 75) claimed to have made the parent compound, CNF, by treatment of cyanogen iodide with silver fluoride. The absorption spectrum and " sodium flame " reaction have also been reported (White and Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 1049: Cosslett, *loc. cit.*). This work is doubtful because the identification of the new fluoride was by molecular-weight determination without any chemical analysis; re-examination of the reaction by Ruff (*Ber.*, 1936, **69**, 193) indicated a mixture of carbon dioxide, silicon tetrafluoride, and perhaps some $(CNF_3)_2$, and more recent work, in which cyanuric fluoride has been prepared, indicates that cyanogen fluoride is a labile intermediate (Kwasnik, F.I.A.T. Final Report No. 1114, 1947, 7; Hückel, *Chem. Abs.*, 1950, **44**, 4359). The preparation of cyanogen fluoride by use of cyanogen chloride with milder fluorinating agents such as plumbous, zinc, mercurous, or antimonous fluoride, has been no more successful. Small yields of gases of low molecular weight, which appeared to be mixtures containing carbon dioxide and silicon tetrafluoride, were obtained. The reaction of cyanogen chloride with silver fluoride in neutral aqueous solution gave carbon dioxide as the only gaseous product. The failure to prepare cyanogen fluoride therefore led to attempts to prepare its derivatives without its own isolation (cf. Part I, *loc. cit.*). A mixture of cyanogen chloride and boron trifluoride passed into anhydrous hydrogen fluoride at 0° left no solid product, and hydrogen fluoride polymerized cyanogen bromide mainly to cyanuric bromide. Fluorosulphonic acid was also used; cyanogen chloride was unaffected at low temperatures, and cyanogen bromide decomposed violently. Finally, bromine trifluoride was shown to bring about carbon–nitrogen bond fission. All carbon was eliminated from cyanogen halides but up to 75% of nitrogen was retained. Cyanogen chloride, bromide, or iodide and boric oxide yielded mixtures of nitrosonium and nitronium tetrafluoroborates with bromine trifluoride, the yield increasing with decreasing volatility of cyanogen halide. The oxygen in the products came from the air and not from the silica reaction flask. Variation of the length and degree of cooling during addition of bromine trifluoride altered the composition of the product. Mixed salts of hexafluoro-phosphates, -antimonates, and -vandates were similarly obtained.

It can be seen that there is no evidence for the cyanogen positive ion in the solid state. However, the correlation of the structure of cyanogen halides with their reactivity to organic molecules provides further evidence of its existence in solution.

Cyanogen chloride or bromide in the presence of aluminium chloride can substitute cyanogen into aromatic nuclei (Friedel and Crafts, *Ann. Chim. Phys.*, 1884, **1**, 528; Scholl and Nörr, *Ber.*, 1900, **33**, 1052, 1055; Karrer and Zeller, *Helv. Chim. Acta*, 1919, **2**, 482; 1920, **3**, 261). Cyanogen iodide, contrary to Karrer and Zeller's implication, produces iodo- and not cyano-derivatives. The yield of iodobenzene from benzene, which was far in excess of 50%, showed that the iodination was not caused by free iodine in equilibrium with cyanogen iodide. The double halides $CNCl,AlCl_3$ and $CNBr,AlBr_3$ also gave cyanobenzene with benzene. The bromide gave a 27% yield in benzene alone, but with nitromethane as solvent the yield increased to 50%. This may have been due to the higher dielectric constant of the reaction medium but was more probably due to the homogeneity of the reaction. The compound $2CNCl,TiCl_4$, however, did not produce any cyanobenzene on reaction with benzene under a variety of conditions. Only cyanuric chloride was isolated. Similarly, thiophen did not give a cyano-derivative but polymerized (compare Hartough, "Thiophene and its Derivatives," Interscience Pub. Inc., New York, 1952, 165). This was not unexpected because titanium tetrachloride is a weak Friedel–Crafts catalyst used for anionic polymerizations or acylations.

That the rate of "cyanosation" was more akin to that of alkylation has been demonstrated by competition reactions. When cyanogen bromide and acetyl bromide were allowed to compete for aluminium bromide in excess of benzene, the product was free from nitrogen. In another experiment cyanogen and propyl bromides in the presence of excess of catalyst competed for benzene in carbon disulphide as diluent. The nitrogen content of the product showed that substitution of propyl and cyano-groups was roughly equivalent.

It should be emphasized that the above experiments show the existence of a positive cyanogen ion only if a positively charged ion is accepted as the reactive entity in the Friedel–Crafts type of reaction. The evidence for this is still far from conclusive, but it does conform with current ideas on aromatic substitution. The actual equilibrium concentration of ions in the low-dielectric media used cannot but be minute, and although it it possible that the mechanisms of reactions are non-ionic, it is more probable that ions of widely varying stabilities are the intermediates in all reactions.

Part of the evidence for the ionic nature of Friedel–Crafts reactions is concerned with the demonstration of the formation of complex anions (*e.g.*, Fairbrother, *J.*, 1937, 503; Karshak and Kolesnikov, *Chem. Abs.*, 1946, **40**, 4033). The work with cyanogen halides could also be taken as evidence for the existence of mixed complex anions. Cyanogen chloride or bromide can be used with aluminium chloride or bromide; cyanogen bromide forms compounds with chlorides as well as bromides, and the conductivity of aluminium bromide in cyanogen chloride solution is only a little less than that of aluminium chloride.

The reactions of cyanogen halides with organometallic compounds can also be explained if a positive cyanogen ion is formed in solution from cyanogen chloride. In the reactions with Grignard reagents it was found that equimolecular amounts of cyanogen chloride and a reagent with a primary alkyl or aryl group gave an alkyl or aryl cyanide as the main product. Cyanogen bromide gave mainly the bromide, whereas cyanogen iodide gave the iodo-compound exclusively (Grignard, *Compt. rend.*, 1911, **152**, 388; 1912, **154**, 361; Grignard and Bellet, *ibid.*, **155**, 44; Grignard, Bellet, and Courtot, *Ann. Chim. Phys.*, 1915, **4**, 28; 1919, **12**, 364; Grignard and Ono, *Bull. Soc. chim.*, 1926, **39**, 1285). The original explanation proposed was in terms of tautomerism of the cyanogen halides. The organic compound was regarded as tautomerizing cyanogen chloride completely to the nitrile form, cyanogen bromide partly to this form, and cyanogen iodide to the *iso*nitrile form. This type of explanation cannot now be regarded as satisfactory because there is definite evidence against tautomerism. If the reaction is considered as a simple ion exchange, however, the results can be understood. Cyanogen chloride in solution can give a positive cyanogen ion, cyanogen iodide a positive iodine ion, and bromine cyanide is intermediate. The reaction with cyanogen chloride can thus be formulated $R^-MgBr^+ + CN^+Cl^- = RCN + MgBrCl$. It appears that BrCN ionizes under these conditions mainly as bromine cyanide compared with cyanogen bromide in the Friedel–Crafts reaction. (All that is implied by the monomeric formula of the Grignard reagent is that a small ionization to carbanions exists in solution.) The substitution of a secondary alkyl or aryl group in the reagent altered the reaction with cyanogen chloride to give about 70% and 50% of chloride in the respective reactions, with about 8—10% of cyanide in both cases. The *cyclo*hexyl group reacted as a secondary alkyl group.

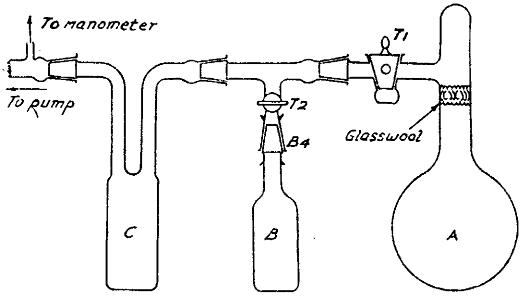
If the above explanation is correct, the latter reactions imply a reverse ionization either of cyanogen chloride or of the Grignard reagent. There is a possibility that carbonium ions are formed in view of the increase in stability of such ions from primary to tertiary groups (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 608; Fairbrother, *ibid.*, p. 765) but further evidence is necessary.

Finally we mention a few experiments illustrating the minuteness of the ionization of cyanogen halides in organic solvents. Neither cyanogen chloride nor iodide solutions in benzene or nitrobenzene gave precipitates of silver halide with silver perchlorate in seven days. With cyanogen iodide and the perchlorate in benzene a complex, mostly of silver cyanide, was precipitated, and when the mixture was heated under reflux a 17% yield of iodobenzene was obtained. From similar experiments with iodine Birkenbach and Goubeau (*Ber.*, 1932, **65**, 395) suggested that iodobenzene was formed by attack of iodonium perchlorate. It is probable that most of the cyanogen iodide reaction results from the positive iodine formed from cyanogen iodide rather than from molecular iodine. Both cyanogen bromide and aluminium bromide solutions in benzene have conductivities not greater than 10^{-9} ohm^{-1} cm.$^{-1}$. Titration of one solution with the other failed to increase this value.

EXPERIMENTAL

Reactions of Cyanogen Chloride with Halides.—Cyanogen chloride stored over phosphoric oxide in the flask *A* (Fig. 1) was distilled on to a weighed amount of halide in flask *B* cooled in liquid air. By manipulation of taps T_1 and T_2 the pressure in the system away from *B* could be kept at 30 cm., and under these conditions distillation was rapid. The taps were then closed and *B* was warmed to 5° and shaken till reaction was complete. Dry nitrogen was passed into the system until the appropriate pressure for distillation was reached, and the excess of solvent distilled into *C* by cooling the latter. With tap T_2 closed the flask was removed and weighed from time to time until constant weight was attained. Finally, solvent in *C* was distilled back into *A*.

FIG. 1.



Analysis of products. These were decomposed *in situ* in a closed apparatus to avoid loss of cyanogen chloride. The chlorine content was determined by precipitation of silver chloride. The cyanogen analysis was effected by alkaline hydrolysis to cyanate and subsequent conversion into ammonia by acid hydrolysis. The ammonia was recovered by distillation. Low results were obtained which were at first attributed to displacement of molecular cyanic acid from solution during the conversion of cyanate into ammonia with strong acid. However, blank experiments with sodium cyanate showed that heating under reflux did not increase the yield of ammonia, and that decreasing the concentration of the mineral acid (0·7N to 0·02N) decreased the yield still further. Previous workers also obtained low results. Lewis and Keyes (*J. Amer. Chem. Soc.*, 1918, **40**, 472) stated that not more than 92% of the ammonia could be recovered. Ruff and Willenberg (*Ber.*, 1930, **73**, 727), analysing bistrifluoromethylamine, converted hydrogen cyanide into ammonia in 93% yield.

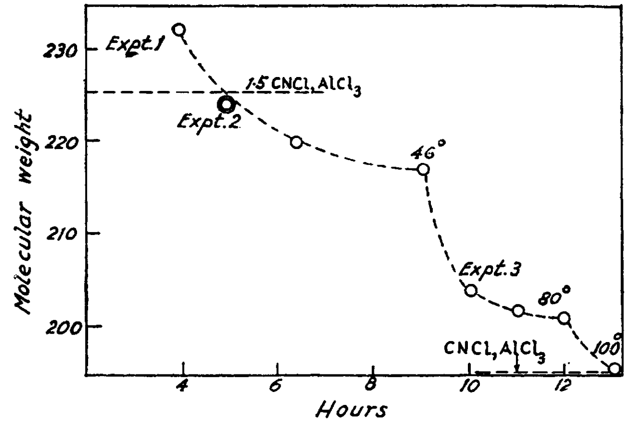
Boron trichloride. A sample was distilled from mercury *in vacuo*. On admixture with cyanogen chloride a white precipitate, soluble in excess of cyanogen chloride, appeared. When most of the solvent had been removed under 30 cm., an exothermic reaction occurred and the white solid became brown. No more cyanogen chloride could be removed even under full vacuum. The solids which remained varied in composition according to the stage at which the exothermic reaction took place. Two products had compositions $BCl_3,1{\cdot}69CNCl$ and $BCl_3,3{\cdot}16CNCl$.

Aluminium chloride. This chloride was readily soluble to give a viscid liquid which changed to a white solid on removal of solvent. The residue was analysed for aluminium and chlorine by dissolving it in ammonia and ammonium nitrate solutions. The precipitated hydroxide was ignited to oxide, and the chloride in the filtrate determined gravimetrically. The residues obtained by removal of cyanogen chloride at room temperature and pressures of about 10^{-5} cm. always retained more than one mole of cyanogen chloride to one of aluminium chloride. The 1 : 1 ratio was approached as the temperature was increased to 100°. Above this temperature the residue darkened and decomposed. Variation of composition with temperature is shown in Fig. 2. The analyses of two high-temperature *products* are given (Found : Al, 14·0, 14·1; Cl, 72·8, 73·7; CN, 13·3%; equiv., 195, 195·5. $CNCl,AlCl_3$ requires Al, 13·8; Cl, 72·9; CN, 13·3%; equiv., 194·8). Products formed at room temperatures had compositions varying from $AlCl_3,1{\cdot}48CNCl$ to $AlCl_3,1{\cdot}64CNCl$.

Titanium tetrachloride. A bulky yellow precipitate was formed on addition of cyanogen chloride to a redistilled specimen of the tetrachloride. A hygroscopic yellow solid remained after removal of excess solvent under 30 cm. The titanium was determined as oxide after precipitation with sodium carbonate (Found : Ti, 15·6; Cl, 68·7; CN, 15·4%; equiv., 316. $2CNCl,TiCl_4$ requires Ti, 15·3; Cl, 68·0; CN, 16·6%; equiv., 313).

Stannic chloride. This chloride was miscible with cyanogen chloride but no solid remained after evacuation under 10 cm. The reaction was also carried out in liquid sulphur dioxide.

FIG. 2.



Stannic chloride (1 ml.) was dissolved in sulphur dioxide (15 ml.), and cyanogen chloride (1 ml.) added. The clear solution was held at −22° for 1 hr., and the solvent evaporated into a trap at −22°. A liquid residue of unchanged chlorides remained.

Antimonic chloride. A white precipitate was formed on addition of cyanogen chloride. The latter was removed under 10 cm. The antimony was determined iodometrically after reduction of a tartrate solution with sulphurous acid. The *compound* was stable at a pressure of 6·5 mm. but began to sublime below 1 mm. (Found : Sb, 33·7; Cl, 59·0; CN, 6·7%; equiv., 361. Calc. for $CNCl,SbCl_5$: Sb, 33·7; Cl, 59·1; CN, 7·2%; equiv., 361). Phosphorus, antimony, and arsenic trichlorides and niobium pentachloride were soluble without reaction and could be recovered unchanged on removal of solvent.

Phosphorus pentachloride, prepared *in situ* from chlorine and the trichloride, was sparingly soluble in cyanogen chloride. Evacuation at 35 cm. removed all solvent. No reaction occurred when the components were heated in a sealed tube.

Auric chloride was prepared in the reaction flask. It was soluble and left a 1 : 1 *compound* after being kept under 18 cm. Products formed at higher pressures had so high a cyanogen chloride pressure that they lost weight continuously. Gold was precipitated by alkaline formaldehyde, and chlorine and cyanogen determined on aliquot portions of the filtrate (Found : Au, 53·6; Cl, 39·2; CN, 6·6%; equiv., 359. $CNCl,AuCl_3$ requires Au, 54·0; Cl, 38·9; CN, 7·1%; equiv., 365).

Platinic chloride was insoluble in and unreactive with cyanogen chloride.

Ferric chloride was readily soluble to give a deep red solution. Removal of excess of solvent at 4—6 mm. gave a yellow-brown 1 : 1 *compound* which readily dissociated at lower pressures.

The iron was determined volumetrically with standard permanganate after precipitation as hydroxide (Found: Fe, 25·5; Cl, 63·2; CN, 10·8%; equiv., 222. $CNCl,FeCl_3$ requires Fe, 25·0; Cl, 63·6; CN, 11·4%; equiv., 224).

Conductivities in Cyanogen Chloride.—Antimony pentachloride. The pentachloride is reported to be a poor or non-conductor (see Gmelin's "Handbuch," 1949, **18**, 443, for references), so its conductivity was redetermined to obtain an absolute value. The antimony pentachloride was purified by trap-to-trap distillation in a tapless apparatus, each trap being sealed off in turn.

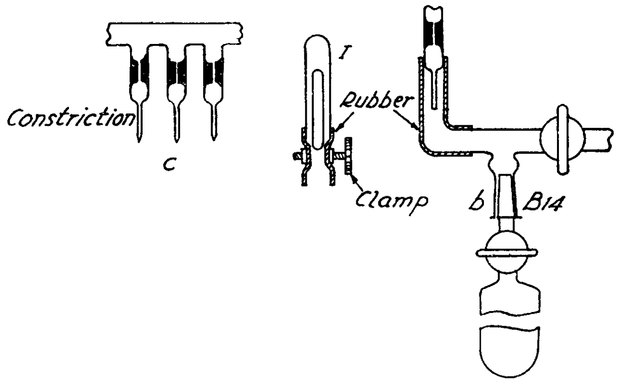
In the absence of a decomposition potential the resistance was determined with direct current. The galvanometer used was calibrated with a standard megohm in place of the cell. Values obtained at 22° are tabulated:

V, v	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00	1·10	1·20
C, μA	0·054	0·096	0·143	0·185	0·233	0·279	0·324	0·368	0·415	0·459	0·504	0·548
V/*C*, μΩ	(1·85)	2·08	2·10	2·16	2·15	2·15	2·16	2·17	2·17	2·18	2·18	2·20

Mean = 2·15 ± 0·03 μΩ; $\kappa = 5{\cdot}75 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$.
Similarly at 8° $\kappa = 4{\cdot}56 \times 10^{-8}$ and at 36° $\kappa = 6{\cdot}11 \times 10^{-8}$.

The conductivity at 0° for 0·0271 mole of pentachloride per kg. of solvent was $4{\cdot}83 \times 10^{-4}$, a value about 400 times that of the pure solvent. The equivalent conductivity of the solution was 17·9. The solution did not obey Ohm's law but it was impossible to obtain a steady decomposition potential. An approximate value of 0·5 v was obtained by taking readings every 2 min.

Fig. 3.



Aluminium trichloride. Hydrogen chloride, dried by concentrated sulphuric acid and phosphoric oxide, was passed over aluminium turnings at 600°. The white sublimate at the cooler end of the tube was quickly melted into ampoules in a stream of nitrogen, and the ampoules were sealed. For purification the ampoules were placed in a vacuum-sublimation line previously outgassed at 400—500°. The first sublimation was carried out at 155—160° and the four successive sublimations at 90—100°. Only a trace of residue remained from the first sublimation. The chloride was finally transferred by vacuum-sublimation to small ampoule tubes. The apparatus described in Part I (*loc. cit.*) was used with the additions shown in Fig. 3. The open tube *H* was fitted with the rubber attachment *I* containing the weighed ampoule which was cleanly marked with a glass knife. The apparatus was evacuated and flamed for some time, then a stream of dry nitrogen, produced from liquid nitrogen and passed through a liquid nitrogen-cooled trap, was allowed into the apparatus. The ampoule was broken in the rubber tubing and dropped into *D*; *I* was removed and *H* quickly sealed while still in the nitrogen stream. The apparatus was evacuated immediately and, apart from bulb *D*, reflamed. Cyanogen chloride was distilled in from *A*, and the apparatus sealed at *E*. The cyanogen chloride was then fractionated as before into *D*, where the solution was prepared and poured into the cell for measurement. The cyanogen chloride was removed and weighed after the experiment by placing rubber tubing over one of the capillary seals between *G* and *H* and distilling the chloride off into a weighing bottle (III*b*) after the seal had been broken. The tap on this weighing bottle had a clamping arrangement which held the pressure generated by the cyanogen chloride at room temperature. By using the capillaries (*C*) part of the cyanogen chloride could be distilled off and a more concentrated solution produced. The results are given in Table 2.

No allowance was made for the volume of vapour in calculation of concentrations, since this is roughly balanced by the retention of some cyanogen chloride by the aluminium chloride when the former is removed for weighing. For example, the volume of apparatus unoccupied by the solution is about 40 ml., which corresponds to 65 mg. of cyanogen chloride at 0° (v.p. ~450 mm.). The weight of aluminium chloride taken (50—100 mg.) would retain 35—70 mg. of cyanogen chloride (the compound remaining at room temperature being assumed to be $AlCl_3,1{\cdot}5CNCl$). The plot of equivalent conductivity against concentration is roughly linear, so the approximate value of equivalent conductivity at infinite dilution is 82 at 0°. The temperature coefficients of conductivity hardly vary with concentration, so the equivalent conductivity–concentration curves at different temperatures will be roughly parallel. After these determinations, the value of the solvent conductivity was redetermined, since the same solvent was being used. The value obtained at 0° was $1{\cdot}60 \times 10^{-6}$, in good agreement with the equilibrium value of $1{\cdot}47 \times 10^{-6}$ obtained previously.

TABLE 2. *Conductivities of aluminium chloride solutions in cyanogen chloride.*

Concn. (C), moles/100 g.	$10^3\kappa$	Temp. (T)	$10^2(\Delta\kappa/\Delta T)$ κ_{mean}	$1000\kappa/C$	Concn. (C), moles/100 g.	$10^3\kappa$	Temp. (T)	$1000\kappa/C$
0·0159 (1) *	1·226	0·0°	5·5	77·2	0·0264 (3)	1·928	0·0°	73·1
	1·296	10·0	—	81·5	0·0442 (4)	3·064	0·0	69·4
0·0249 (2)	1·867	0·0	5·8	74·8	0·0967 (5)	5·08	0·0	52·6
	1·973	10·0	—	79·3				

* Nos. 2, 4, and 5 were obtained in a single experiment.

Aluminium bromide. The bromide was prepared by direct union of the elements, and distilled from excess of aluminium as a colourless liquid. Final purification was by vacuum-sublimation. The procedure was then the same as with aluminium chloride solutions. The temperature coefficient (see Table 3) was about the same as with aluminium chloride solutions but the conductivity values were lower. Again the equivalent conductivity–concentration curve was roughly linear and almost parallel to the chloride curve. The equivalent conductivity at infinite dilution was 74.

TABLE 3. *Conductivities of aluminium bromide solutions in cyanogen chloride.*

C, moles/1000 g.	$10^3\kappa$	Temp.	$1000\kappa/C$	C, moles/1000 g.	$10^3\kappa$	Temp.	$1000\kappa/C$
0·0170	1·167	0°	68·5	0·0334	2·120	0°	63·5
	1·237	10	72·8	0·0814	4·005	0	49·2

Ferric chloride. Chlorine, dried by passing through concentrated sulphuric acid and phosphoric oxide, was passed over heated iron wire. The ferric chloride sublimed to the cooler part of the tube, whence it was resublimed in a stream of chlorine and sealed in the tube. For purification the sample was sublimed *in vacuo*, first at 250°, then at 150—180°. Iridescent green crystals remained. The conductivity (see Table 4) was determined as described above. The equivalent conductivity–concentration curve was non-linear. The extrapolated equivalent conductivity at infinite dilution was *ca.* 82.

TABLE 4. *Conductivities of ferric chloride solutions in cyanogen chloride.*

C, moles/1000 g.	$10^3\kappa$	Temp.	$10^2(\Delta\kappa/\Delta T)$ κ_{mean}	$1000\kappa/C$	C, moles/1000 g.	$10^3\kappa$	Temp.	$10^2(\Delta\kappa/\Delta T)$ κ_{mean}	$1000\kappa/C$
0·0292	1·91	0·0	8·9	65·4	0·0518	2·85	0·0°	—	55·0
	2·08	9·6	—	71·2	0·127(3)	4·38	0·0	6·2	34·4
						4·66	10·0	—	36·6

Arsenic trichloride. The trichloride was purified by vacuum distillation in an all-glass apparatus. The values shown in Table 5 were obtained at 0° (κ_s, the conductivity of the solvent, was taken as $1{\cdot}60 \times 10^{-6}$). The rough value for the equivalent conductivity at infinite dilution was 0·12.

TABLE 5. *Conductivities of arsenic trichloride solutions in cyanogen chloride.*

C, moles/1000 g.	$10^6\kappa$	Equiv. conductivity, $1000(\kappa - \kappa_s)/C$
0·0154	4·60	0·195
0·0577	9·78	0·142

Electrolysis in Cyanogen Chloride Solutions.—The apparatus, shown diagrammatically in Fig. 4, was used as follows. Cyanogen chloride was distilled into *A* and weighed. The weighed flask was attached to the apparatus which contained the solid sample and magnetic hammer in *B*, and the whole apparatus evacuated through T_2. The contents of *B* were sublimed into *C* after the ampoule had been broken, and *B* was sealed at the constriction. The cyanogen chloride was then distilled into *C*, and the constriction *a* sealed. The solution was made in *C* which could be rotated freely about *F*. Finally, the solution was poured in the cell and the last seal made at *f*. The solution was electrolysed at 20—40 mA at 0°, the amount of electricity being measured by a copper coulometer in series. At the end of electrolysis the wide-bore tap T_1 was closed, and the gas sample sealed off. Samples of the electrolyte were poured into the calibrated tubes *E* and *D*. The solvent was removed *in vacuo*, and the solid remaining was analysed for the particular metal. The electrodes were also weighed before and after the experiment.

Electrolysis of aluminium chloride solution. Platinum cylinder electrodes were employed. At the end of the electrolysis the liquid in the anode was yellow and separated by a sharp boundary from the remaining brown solution. The original solution was colourless. Two samples were removed from each electrode chamber. The volume of samples was 21·0 ml., and the residual volume 8·9 ml. The aluminium content was determined as alumina after dissolution of the dried samples in hydrochloric acid and precipitation as aluminium hydroxide. The values obtained by the passage of 0·00876 F were :

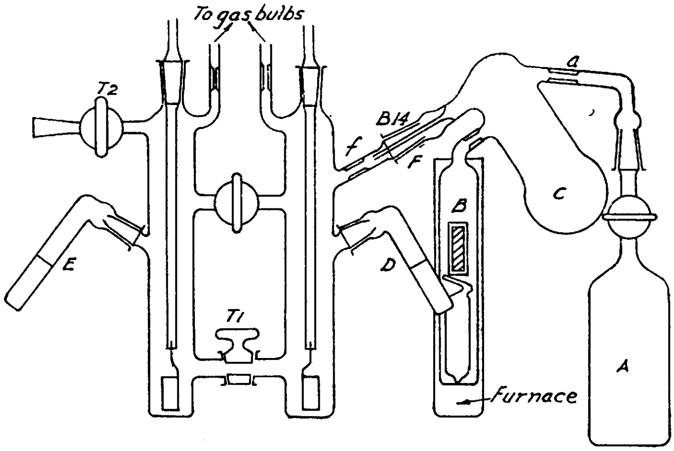


FIG. 4. *Electrolysis apparatus.*

	Concn. (mg. Al/ml.)		Concn. (mg. Al/ml.)		Concn. (mg. Al/ml.)
Original solution...	10·87	Anode sample 1 ...	9·78	Cathode sample 1	8·62
		,, 2 ...	11·57	,, 2	8·92

The cathode lost 5·3 mg., and the anode 0·9 mg. in weight. A gas evolved at the cathode was shown to be cyanogen chloride, possibly produced by local heating. The molecular weight of the gas, determined by Regnault's method in a calibrated bulb, was 61·6 (Calc. for CNCl: 61·5). The absence of chlorine was indicated by the fact that the mercury in the manometer was unattacked, and the absence of cyanogen by the absence of cyanide after alkaline hydrolysis. (Sufficient time was allowed for complete hydrolysis.)

The cyanogen chloride was confirmed by measuring the amount of sodium hydroxide needed for hydrolysis, and the amount of chloride formed. The possibility that cyanogen and chlorine were formed in equal amounts and recombined in the presence of aluminium chloride was unlikely, especially since no gas was evolved at the anode.

Therefore electrolysis of aluminium chloride in cyanogen chloride leads to transport of aluminium in an anion. If this anion is singly charged and the transport number is assumed to be 0·5, then the amount of current passed could transfer 118 mg. of aluminium. The approximate weight of aluminium transferred, 58 mg., is the product of the electrolyte volume and the mean difference in the electrode chambers. The change in colour on electrolysis and the large amount of yellow water-insoluble solid left on removal of solvent showed that further reactions were taking place. The possibility of ionic polymerization, for example, cannot be disregarded.

Electrolysis of ferric chloride solution. (i) With platinum electrodes. The figures obtained in a transport experiment were as shown below. The iron was determined, after dissolution in sulphuric acid and reduction, by potassium permanganate standardized against iron wire. A gas sample (*M*, 61·4) again proved to be cyanogen chloride. The cathode and anode lost 0·1 and 1·0 mg., respectively.

	Concn. (mg. Fe/ ml.)		Concn. (mg. Fe/ml.)		Concn. (mg. Fe/ml.)
Original solution...	6·94	Anode sample 1 ...	6·76	Cathode sample 1	5·64
		,, 2 ...	6·93	,, 2	6·94

These results are not as definite as with the aluminium chloride since all the concentrations found were no greater than that of the original solution. About 6 ml. of solution were not analysed. This includes the lower layer of the anode which would be above the original concentration if the trend for increase in concentration with depth, found in all these experiments, were maintained. No iron was deposited on the electrodes.

(ii) With silver electrodes. Long silver cylinders whose ends were well above the electrolyte level were used. They were silver-soldered to tungsten wires sealed through Pyrex tubing. In this experiment an attempt was made to account for all the iron, although the nature of the electrode deposits only allowed of semi-quantitative observations.

Passage of current reduced the intense red colour around the cathode, and as electrolysis proceeded a sharp boundary appeared. The liquid at the cathode went through yellow to colourless, and that at the anode also became lighter in colour although it was still dark red at the end of the experiment. A white deposit settled on the anode at the red–colourless interface, but only traces were carried over into the anode compartment. The deposit at the cathode was almost black. When the solution at the cathode became almost colourless gas evolution commenced. The current passing through the cell decreased throughout the experiment from 40 mA at 50 v to 15 mA at 230 v. Analysis of solution samples gave the following values. These alone showed that depletion of iron at the cathode was not due to transport to the anode, and this was confirmed by the following analysis.

	Concn. (mg. Fe/ml.)		Concn. (mg. Fe/ml.)		Concn. (mg. Fe/ml.)
Original solution...	11·35	Anode sample 1 ...	3·79	Cathode sample 1	0·31
		,, 2 ...	8·42	,, 2	0·23

The cathode deposit was carefully scraped off, after removal of solvent from the remaining solution (5·7 ml.) *in vacuo*. The black solid was dried at 120° to remove traces of cyanogen chloride, and then extracted with ammonia to remove silver chloride carried over from the anode (this amounted to 2·3%). Chloride was determined by adding silver nitrate, and the iron in the ammonia-insoluble residue dissolved in sulphuric acid and titrated with permanganate after reduction. This titration was not satisfactory as the end-point faded, so it had to be checked gravimetrically. This fading may have been due to oxidation of paracyanogen present. The distribution of iron was as follows:

	Vol. × Fe content/ml.	
Anode limb:		
Sample 1	5·09 × 3·79	= 19·3
,, 2	5·40 × 8·42	= 45·5
Remainder	1·2 × 6·11 (mean of 1 and 2)	= 7·3
Cathode limb:		
Sample 1	5·31 × 0·31	= 1·6
,, 2	4·87 × 0·23	= 1·1
Remainder, including tap bore	3·6 × 0·27 (mean of 1 and 2)	= 1·0
Cathode deposit		= 195
Anode deposit		= 12
	Total	= 283 mg.

The iron introduced as ferric chloride was 300 mg., in good agreement with the above value in view of the difficulty of quantitative transfer of electrode deposits.

The transfer of iron to the cathode limb was also shown by comparison of the original and final iron contents. The agreement between the gain and loss of iron was a confirmation of the above analysis.

	Cathode	Anode
Original content of iron (mg.)	140	138
Final ,, ,, ...	198	81
Change in ,, ,, ...	58	−57

From the figures for the cathode deposit analysis (AgCl, 2·3; Cl, 30·8; Fe, 34·1%) it can be seen that Fe/Cl = 1/1·42, and hence the deposit must have contained some free iron. There was also a residue of 33% which, by its solubility in concentrated sulphuric acid and reprecipitation as a black powder on rendering the solution alkaline, was probably paracyanogen. The gas collected, although consisting mainly of cyanogen chloride, contained a small proportion of cyanogen (*M*, 61·0; positive test for cyanide on alkali hydrolysis). The cathode lost only 20 mg. in 9·5 g. after all the deposit had been cleaned off with dilute ammonia. The anode deposit was analysed similarly (AgCl, 79%; Fe, 8·2 = $FeCl_3$, 24%). The absence of cyanide was shown by heating the solid, which would decompose any silver cyanide to silver, and testing the residue for silver after extraction of silver chloride with ammonia. The anode was also cleaned with ammonia and the loss of silver was found to be 539 mg. The attack was over the area of deposit.

The 0·1390 g. of copper deposited in the coulometer was equivalent to 472 mg. of silver, in rough agreement with the silver converted into silver chloride. Hence the net result of electrolysis was deposition of iron and formation of cyanogen and its polymer at the cathode, and liberation of chlorine at the anode.

Electrolysis of an antimonic chloride solution. A qualitative experiment using a platinum cathode and a silver anode showed that chlorine was formed at the anode and cyanogen at the cathode. The cell was smaller than that described, because the pentachloride had only a limited solubility in cyanogen chloride and the electrodes had to be closer together. The use of different electrodes was necessary because of mixing of the electrode deposits. The silver chloride formed could only have come from the anode.

Reactions of Cyanogen Bromide with Aluminium and Stannic Bromides.—10 Ml. of an 8% solution of cyanogen bromide in light petroleum (b. p. 60—80°) (dried by distillation from P_2O_5) gave an immediate precipitate on addition to a solution of 1 g. of aluminium bromide in light petroleum. Further additions of cyanogen bromide gave no more precipitate. The deposit was filtered off in a closed apparatus protected from atmospheric moisture, washed with light petroleum, and dried *in vacuo*. Aluminium was determined as its oxide, bromine as silver bromide after decomposition with sulphurous acid, and cyanogen bromide by titration in acid solution with thiosulphate (Found: Al, 7·22; Br, 85·2; CNBr, 28·7. $CNBr,AlBr_3$ requires Al, 7·24; Br, 85·8; CNBr, 28·5%). The same *compound* was precipitated when diethyl ether, or, less satisfactorily, when carbon tetrachloride or ethylene dibromide solutions were used. It was soluble in ethanol, nitromethane, and nitrobenzene. It darkened at about 90° and melted at 119—120° to a dark brown liquid.

Stannic bromide gave no precipitate under the above conditions.

Conductivities of aluminium and stannic bromides in cyanogen bromide. The conductivity cell was connected to a mixing flask and ampoules of cyanogen bromide and the other bromide. The former ampoule was broken magnetically, and its contents were distilled *in vacuo* into the mixing flask, where it was melted and poured into the cell. After the solvent conductivity had been checked, the second ampoule was broken, and both halides were distilled into the mixing chamber, whence the solution was poured into the cell.

When 1·58 moles of aluminium bromide per kg. of solvent were used, dissolution was incomplete. The conductivity increased from $3·6 \times 10^{-5}$ at 56·4° to $8·3 \times 10^{-3}$. A more dilute solution (0·0111 mole/kg.) which was only slightly brown gave a specific conductivity of $9·55 \times 10^{-4}$ and an equivalent conductivity of 83 after allowance for solvent conductivity.

Stannic bromide gave a colourless solution in cyanogen bromide. The conductivity of a solution of 0·0276 mole/kg. of solvent fell rapidly to $2·53 \times 10^{-3}$ at 55·8° and remained steady for a few hours although the solution became yellow. The value increased to $5·0 \times 10^{-3}$ after one day.

Attempts to prepare Cyanogen Fluoride and its Derivatives.—Cyanogen chloride was heated in sealed tubes or continuous-flow systems with ZnF_2, HgF, PbF_2, and SbF_3 at 150—250°. The main effect was to polymerize the cyanogen chloride. The gases isolated were chiefly carbon dioxide and silicon tetrafluoride. A nitrogen-containing gas, isolated when mercurous fluoride was used, was traced to small amounts of nitrate remaining from the preparation of the fluoride.

Reaction of cyanogen chloride with aqueous silver fluoride solutions gave carbon dioxide. Although precipitation of silver chloride was immediate, it was only reasonably complete in 10 hr. in neutral solution. The hydrolysis of cyanogen chloride in this time is approx. 20% (Eden and Wheatland, *J. Soc. Chem. Ind.*, 1950, **69**, 166). The gas evolved on heating was mainly carbon dioxide (*M*, 43·5; CO_2 content 95% determined with standard barium hydroxide solution).

Reactions with Bromine Trifluoride.—Cyanogen bromide or iodide and excess of boric oxide gave white solids, which retained most of the nitrogen, when treated with the trifluoride in the usual way (Woolf, *loc. cit.*). In order to test for carbon in these compounds, potassium was vacuum-distilled at 400° into suitable tubes. The compound and potassium fluoride were added, and the evacuated tubes heated at temperatures varying from 200° to 400°. No free carbon was formed, and no cyanide could be detected in the hydrolysate even by the sensitive Aldridge test (*Analyst*, 1945, **70**, 474). Thermal decomposition of the compounds with potassium fluoride yielded mainly nitrogen trioxide and traces of nitrogen- and fluorine-containing gases. (These gases could have been formed by the attack of NOF and NO_2F on glass at the temperatures used.)

Analysis of a product from cyanogen iodide showed it to be an equimolecular mixture of nitrosyl and nitryl fluoroborates (Found: N, 11·25; F, 61·1. Calc. for $NOBF_4 + NO_2BF_4$: N, 11·1; F, 61·7%). 0·0706 g. of the compound, after dissolution in water and oxidation of nitrite to nitrate with potassium permanganate and dilute sulphuric acid, gave 0·428 g. of a nitron precipitate (Calc. for above equimolar mixture: 0·434 g.). The variation of fluorine content from 60·7 to 62·6% in different experiments corresponded to nitrosyl/nitryl ratios of 0·82—2·22. The nitrogen retention varied from 63 to 70% with cyanogen iodide, and was around 50% with cyanogen bromide. Similar results were obtained with vanadium and phosphorus oxides in place of boric oxide. Hexafluoro-vanadates and -phosphates were formed. With antimony salts the results were more complex. The products contained bromine, presumably as SbF_5,BrF_3 (Woolf and Emeléus, *J.*, 1949, 2865). The amount of bromine in the products increased with the volatility of the cyanogen halide used. With stannous chloride or stannic fluoride and cyanogen bromide only the decomposition products of $SnF_4,2BrF_3$ could be isolated.

Ionisation in Organic Solvents.—Conductivities of cyanogen bromide and aluminium bromide in benzene. "AnalaR" benzene, purified by fractional freezing, was distilled from calcium hydride on to weighed ampoules of cyanogen bromide or aluminium bromide. Solution was effected by passage of dry nitrogen, and the solution blown over into the conductivity cell. Precautions taken included use of dry nitrogen evolved from the liquid, and avoidance of all grease and ingress of moisture. Resistance was measured on a D.C. circuit using a 120-v dry battery and a galvonometer. The results obtained were that a 0·0936M-solution of cyanogen bromide had a conductivity of $2·5 \times 10^{-9}$, a 0·0217M-solution of aluminium bromide one of $0·82 \times 10^{-9}$. Titration of an aluminium bromide solution with one of cyanogen bromide did not alter the conductivity; the final value did not exceed $1·7 \times 10^{-9}$.

Reactions with Silver Perchlorate.—The salt was prepared by dissolving silver oxide in perchloric acid and evaporation at 120° (Found: Ag, 51·5. Calc. for $AgClO_4$: Ag, 52·0%).

Cyanogen chloride. Equivalent amounts of the perchlorate and cyanogen chloride were kept in benzene. The chloride was measured out by volume and condensed into a small ampoule broken by shaking in the flask. The benzene was distilled from phosphoric oxide directly on to the silver perchlorate. No precipitate appeared after 7 days. The experiment was repeated in nitrobenzene solution with the same result.

Cyanogen bromide. Similar experiments gave no precipitates after 10 days.

Cyanogen iodide. Separate solutions of silver perchlorate and cyanogen iodide in benzene were mixed. Immediate precipitation occurred. The precipitate was heated at 100° *in vacuo* to remove ICN; the residue was a mixture of silver perchlorate, silver cyanide, and some cyanogen iodide. No silver iodide was formed.

The reaction with the solvent was examined after a mixture had been refluxed for 12 hr. The benzene layer was washed with sulphurous acid, then with water, and dried ($CaCl_2$). On distillation, iodobenzene was recovered in 17% yield (b. p. 186°, uncorr., d_4^{20} 1·825. Cf. PhI, b. p. 188°, $d_4^{18·5}$ 1·832; PhCN, b. p. 191°, *d* 1·01).

Reaction of Double Halides with Benzene.—$2CNCl,TiCl_4$. Most of the compound dissolved on boiling. On cooling, yellow crystals appeared. After 3 hours' refluxing the solution was poured into water, and the clear solution extracted with ether, dried ($CaCl_2$), and distilled. No phenyl cyanide but cyanuric chloride was isolated. The experiment was repeated with addition of calcium carbonate to remove any acid formed. Again, no cyanogen substitution compound was formed.

$CNCl,AlCl_3$. This formed cyanobenzene only after refluxing. A slight reaction took place in the cold.

$CNBr,AlBr_3$. The compound (2·9 g.) was refluxed with benzene (15 ml.). The residue was decomposed with water (15 ml.), extracted with ether, dried, and distilled, 0·22 g. of cyanobenzene being isolated (yield 27%). 2·8 G. of the compound and 3 ml. of benzene, refluxed with 35 ml. of nitromethane, gave a 50% yield.

Friedel–Crafts reactions. Cyanogen iodide (0·2 mole) and aluminium chloride (0·2 mole) were refluxed with 150 ml. of benzene. A heavy precipitate remained after 9 hours' heating. The residue was poured into sulphurous acid, washed with sodium carbonate solution, then water, and dried. On distillation, crude iodobenzene (b. p. 187°) was recovered in 83% yield, some of which was redistilled under reduced pressure for measurement (Found : d_4^{17} 1·834, n_D^{20} 1·620; cf. PhI, $d_4^{18 \cdot 5}$ 1·832, $n_D^{18 \cdot 5}$ 1·6214). When an equivalent amount of iodine (36 g.) was used only 8 g. of crude iodobenzene were isolated (yield 30%).

Competition reactions. Acetyl bromide (0·05 mole), cyanogen bromide (0·05 mole), and aluminium bromide (0·06 mole) were refluxed with benzene. The residue was decomposed with water, extracted with ether, dried, and distilled. All the distillate above 100° was collected. Analysis showed absence of nitrogen.

Bromobenzene (0·05 mole), cyanogen bromide (0·05 mole), benzene (0·05 mole), and aluminium chloride (0·10 mole) were refluxed with carbon disulphide as diluent. After treatment as above, the distillate above 150° contained N, 6·4%, equivalent to a mixture of 47% of cyanobenzene and the rest *iso*propylbenzene, if these were the products. No fraction corresponding to the latter (b. p. 153°) could be isolated, but the results show that roughly 38% of nitrogen from the cyanogen bromide enters the organic molecule.

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