

839. *The Cyanogen Halides. Part I. A Comparison with the Interhalogen Compounds and Nitrosyl Halides.*

By A. A. WOOLF.

The conductivities of the liquid cyanogen halides, and their reactions with metals and organic compounds in the absence of a solvent, are explained in terms of their dissociations to free halogens. Part of the conductivity of the liquid cyanogen halides is due to self-ionization, and attempts to stabilize this ionization by polyhalide formation are described.

STUDIES of the cyanogen halide structures by chemical methods have often led to contradictory results. The main controversy has turned on their nitrile or isonitrile structure. Electron-diffraction and microwave-spectral studies, however, have settled unequivocally the linear X-C-N structure in the gas phase, and an X-ray diffraction study the molecular lattice of at least cyanogen iodide in the solid state (Beach and Turkevich, *J. Amer. Chem. Soc.*, 1939, **61**, 299; Schulman and Dailey, *Phys. Review*, 1950, **78**, 145; Ketelaar and Zwartsenberg, *Rec. Trav. chim.*, 1939, **58**, 558). Now that the structures are definitely established it is of interest to correlate structure with reactivity in contrast to the reverse procedure of earlier investigators. Fairbrother (*J.*, 1950, 180) has already shown that the reactions of cyanogen halides in solution are explicable by a solvolytic ionization, and that the different behaviour of cyanogen chloride and iodide is not due to any structural difference in the free molecules, but to the solvent-solute interaction. In contrast, some of the reactions of cyanogen halides in the absence of a solvent are here considered, and it is shown that they are governed by the dissociation of the halides, rather than by their ionizations. The binary interhalogen compounds and nitrosyl halides react similarly and a comparison is included.

The possibility of ionic reactions in the absence of solvent, brought about by ionic species present in the liquid cyanogen halides, cannot be neglected. The ionization of related groups of halides should be related to the bond strength directly concerned, the ease of ionization decreasing with bond order. The direction of polarity is not considered at this stage. The relevant bond lengths are collected in Table I.

TABLE I. *Calculated and experimental bond lengths of halides.*

Compound	Bond	Bond length, Å		A-B *
		Sum of single-bond covalent radii, A	Exptl., B	
ICI	I-Cl	2.32	2.32	M 0.00
FCI	F-Cl	1.63	1.63	M 0.00
BrF	Br-F	1.78	1.76	M -0.02
NOCl	N-Cl	1.69	1.95	E -0.26
NOBr	N-Br	1.84	2.14	E -0.30
CNCl	C-Cl	1.76	1.63	M 0.13
CNBr	C-Br	1.91	1.79	M 0.12
CNI	C-I	2.10	2.00	M 0.10

* M = Microwave data. E = Electron-diffraction data.

The calculated single bond lengths are taken from either Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, 1950, or Wells, "Structural Inorganic Chemistry," Oxford University Press, 1950.

It can be seen that with the interhalogen compounds the links are normal single bonds, the mean of the component halogen radii. In the cyanogen halides, however, the carbon-halogen bond is appreciably shorter than the single-bond length, and the bond order is greater than unity. The opposite holds with the nitrosyl halides, although it should be remembered that these molecules are not linear. One might therefore expect ionization to increase in the order cyanogen halides, interhalogen compounds, nitrosyl halides.

It is possible to assess the ionization of substances by comparison of their conductivities in the liquid state if the differences in ionic mobility are of lower order than the differences in the conductivities. In Table 2 the available conductivity values are given to the nearest power of 10. The fact that these figures do not substantiate the simple relation between

ionization and bond order may be due to neglect of intermolecular in comparison with intramolecular forces. The conductivity values, however, are not those of pure compounds. The maximum dissociation can be calculated from the available thermodynamic data. The values for the interhalogen compounds are taken from Greenwood (*Rev. Pure Appl. Chem. Australia*, 1951, 1, 84), and other values from "Selected Values of Thermodynamic Constants" (National Bureau of Standards, 1952), except that of cyanogen bromide, for which

TABLE 2. Conductivities of halides.

Com- pound	$\kappa \times 10^6$, ohm ⁻¹ cm. ⁻¹	Temp. of measurement	M. p.	Com- pound	$\kappa \times 10^6$, ohm ⁻¹ cm. ⁻¹	Temp. of measurement	M. p.
NOCl ¹	1	-20°	-64°	CNCl	1	0°	-6.5°
ICl ²	1000	35	27	CNBr	100	58	52
IBr ³	100	40	36	CNI	1000	150	146

¹ Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, 70, 1964. ² Cornog and Karges, *ibid.*, 1932, 54, 1882. ³ Bruner and Beckier, *Z. Elektrochem.*, 1912, 18, 368.

the heat of formation is assumed to be the mean of the values for the iodide and the chloride. More recent data on the heats of formation of the cyanogen halides will be discussed in a forthcoming publication, but the old values are employed, it being borne in mind that errors of an order of magnitude of 1—2 kcal. are possible.

The values are summarized in Tables 3 and 4. The most obvious difference between the interhalogen halides and the nitrosyl and cyanogen halides is the large positive value for the free energy, with respect to the elements, of the latter compared with the small negative values of the former. The free-energy values with respect to the halogen and pseudo-halogen reduce this large difference, and negative values are obtained for the dissociation energies of nitrosyl halides. With the cyanogen halides, however, only the chloride has a negative value; both the iodide and the bromide at equilibrium are considerably dissociated.

TABLE 3. Heats of formation and free energies of halides formed from elements in their standard states at 25° (kcal./mole).

Compound	ΔH	ΔG	Compound	ΔH	ΔG
CNI (g)	54.6	47.7	ICI (g)	-3.31	-3.71
CNI (s)	40.4	42.6	ICI (s)	-8.04	-3.25
CNCl (g)	34.5	32.9	BrCl (g)	-6.8	-1.2
NOCl (g)	12.75	15.86	FCl (g)	-12.3	-12.6
NOBr (g)	19.56	19.70	FBr (g)	-17.0	-17.4
			IBr (g)	-1.38	-1.79

TABLE 4. Free energies of dissociation of halides at 25° (kcal./mole).

	Equilibrium	ΔG	$\log_{10} K$
ICN (g)	$\rightleftharpoons \frac{1}{2}I_2 (g) + \frac{1}{2}(CN)_2 (g)$	-7.7	5.6
ICN (s)	$\rightleftharpoons \frac{1}{2}I_2 (s) + \frac{1}{2}(CN)_2 (g)$	-7.2	5.3
BrCN (g)	$\rightleftharpoons \frac{1}{2}Br_2 (g) + \frac{1}{2}(CN)_2 (g)$	-4.9	3.6
CNCl (g)	$\rightleftharpoons \frac{1}{2}Cl_2 (g) + \frac{1}{2}(CN)_2 (g)$	2.5	-1.8
NOCl (g)	$\rightleftharpoons NO (g) + \frac{1}{2}Cl_2 (g)$	4.86	-3.57
NOBr (g)	$\rightleftharpoons NO (g) + \frac{1}{2}Br_2 (g)$	1.02	-0.74
Calc. using ΔG for NO		20.7	—
" " "	(CN) ₂	70.8	—
And assuming ΔG for BrCN (g)		40.3	—

The free energies of dissociation of the interhalogen compounds are given by the ΔG values of Table 3 with the sign reversed.

In practice, the equilibria are not attained. Cyanogen iodide and bromide are snow-white solids with no trace of free iodine or bromine; when they are molten the amount of free halogen as judged by colour is quite small. Even cyanogen chloride is not apparently at equilibrium. It can be stored for months over mercury without attacking the metal, whereas nitrosyl chloride, with an equilibrium constant 150 times as small, readily attacks the metal. This lack of equilibration of the cyanogen halides is in marked contrast with that of the other halides, for which the free-energy values calculated from equilibrium experiments are in such good agreement with those obtained from combined thermochemical and spectroscopic data.

The conductivity data obtained with the cyanogen halides can now be considered in more detail in the light of the above dissociations. The conductivity value obtained for cyanogen chloride depended on the drying agent used. Specimens dried by both calcium chloride and magnesium perchlorate had higher conductivities than those dried by phosphoric oxide. All values increased with time, but with phosphoric oxide drying, a steady value, about 50% greater than the original, was obtained after 10 hours; all fell within the range $1-3 \times 10^{-6}$ at 0° . Cyanogen bromide, which could not be dried with the pentoxide, was dried in the vapour phase over magnesium perchlorate previously dehydrated at 250° *in vacuo*. This treatment is presumably almost as effective as treating molten cyanogen bromide with the pentoxide. Even with this drying, however, the conductivity was still increasing after 2 days. Cyanogen iodide vapour was also dried by magnesium perchlorate. The conductivity increased rapidly on melting, and free iodine, which remained on freezing, was liberated. This process could be repeated with a gradual increase in the amount of iodine left in the solid. These phenomena are explicable in terms of the dissociation if it be assumed that the rate of attainment of equilibrium is a function of the distance from equilibrium in the cyanogen halide series. With cyanogen chloride a steady value is attained because the maximum dissociation is small, less than 1%. The failure of cyanogen bromide to attain a steady value indicates a slow dissociation into bromine and cyanogen, as also shown by the final light brown colour of the melt, compared with the initially colourless liquid. A true equilibrium is not attainable because the bromine formed can polymerize cyanogen bromide. It is unlikely that any cyanuric bromide formed would increase the conductivity of cyanogen bromide. The conductivity of 10^{-2} for cyanogen bromide reported by Glockler (*Proc. Nat. Acad. Sci.*, 1926, **12**, 522) is that of an obviously impure specimen. Cyanogen iodide is so far from equilibrium that iodine is formed continuously. The high conductivity may be associated with the high conductivity of molten iodine, which is regarded as possessing metallic, in addition to ionic, conduction in the melt. The positive temperature coefficients of conduction for both cyanogen chloride and bromide indicate that electronic conduction is not here involved. The instability of molten cyanogen iodide precludes any measurement of its temperature coefficient.

The conductivity of the interhalogen compounds must also be considered from the viewpoint of dissociation into their constituents. It is known that they readily attain their equilibrium state, so it may well be that the extremely reproducible conductivity of iodine monochloride, for example, is due not only to the dissociation $2\text{ICl} \rightleftharpoons \text{I}^+ + \text{ICl}_2^-$, but also to the ionization of dissociated iodine in a solvent (Cornog and Karges, *loc. cit.*; Fialkov and Goldman, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 910; Fialkov and Shor, *ibid.*, 1948, **18**, 14; Greenwood and Emelús, *J.*, 1950, 987). If the iodine were appreciably ionized, its contribution to the total ionization could be comparable to that from the self-ionization of the solvent. With iodine monobromide, the more extensive dissociation would be expected to make a greater contribution to the conductivity. In other words, the measured conductivities of the interhalogen compounds are greater than the values for the "pure" compounds by an amount which varies with the dissociation of the compounds, the ionization of the dissociation products, and the products' reaction with the solvent.

This dissociation of the halides can affect their reactions in the absence of solvents. The reactions of molten interhalogen compounds with metals have been quoted as evidence for their mode of ionization. Gutmann, for example, referring to iodine monochloride, states that "the metal unites with the negative part of the solvent with separation of the positive portion" (*Z. anorg. Chem.*, 1951, **264**, 169). The implication that an ionic mechanism is operative is doubtful, and it is more reasonable to assume that, with iodine chloride and bromide, a molecular halogenation occurs in a direction governed by the relative rates of halogenation. This direction can be predicted independently of the mechanism by the overall free-energy change and is in the order chloride, bromide, iodide, cyanide. (The thermal decompositions of polyhalides follow a similar sequence.)

Hence, cyanogen iodide should iodinate, and cyanogen bromide brominate, metals, even though both can ionize as cyanides (Fairbrother, *loc. cit.*). This type of reaction was attempted with only a few metals, since comparatively few form well-defined cyanides.

Although the reactions were complicated by the polymerization of the cyanogen halides no cyanide formation could be detected.

The dissociation of cyanogen bromide may also be involved in its reaction with sodium atoms and suggests an alternative explanation to that proposed by Evans and Walker (*Trans. Faraday Soc.*, 1944, **40**, 384) to explain the small difference in activation energies between the "sodium flame" reactions of cyanogen bromide and chloride.

Further examples which can be explained by reactivity of the dissociation products are provided by some reactions with organic compounds. Cyanogen chloride and bromide do not react with ethylene, but cyanogen iodide forms di-iodoethylene. This has been attributed to a direct iodination which can proceed to completion (Mooney and Reid, *J.*, 1931, 2597). The bromination of benzene and naphthalene above 200°, and of phenol and resorcinol at 130°, by means of cyanogen bromide is probably a direct bromination by bromine (Merz and Weith, *Ber.*, 1877, **10**, 746; Scholl and Norr, *Ber.*, 1900, **33**, 1555).

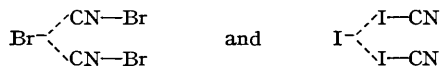
The conductivity of the cyanogen halides, however, cannot be entirely due to dissociation; there must be some self-ionization. Recent work with iodine and nitrosyl chlorides has demonstrated their combination with halides of Group I and II elements, or analogous radicals, to form compounds which can ionize as "bases," and with halides of Groups III, IV, and V to those which can ionize as "acids" (Gutmann, *Z. anorg. Chem.*, 1951, **264**, 151; Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143). Amphoteric and other behaviours provide exceptions to this generalization. A study was made of the combination of cyanogen halides with other halides to see whether ionization could be induced in the absence of a solvent. The four ways in which cyanogen bromide can react with alkali halides are:



Consideration of the free-energy changes shows that reaction (2) is negligible and reaction (4) is almost complete, and experiment proves that (4) is the preferred reaction with cyanides and that (2) does not occur. This would be convincing evidence for an ionization CN^+Br^- if reaction (1) also occurred, but it is found that two moles of cyanogen bromide combine with one of an alkali bromide. [Combination occurred with the bromide of the large tetramethylammonium ion but not with potassium bromide. This is usual for polyhalide formation although there are exceptions (Duncan and Cremer, *J.*, 1933, 181; Emeléus and Sharpe, *J.*, 1949, 2206).]

With cyanogen iodide, the reaction of type (2), but with iodides instead of bromides, is feasible but (4) should be negligible. In practice, both reactions proceed to some extent. In fact, paracyanogen is formed, so calculations based on cyanogen formation can only be approximate. Mathewson and Wells (*Amer. Chem. J.*, 1903, **30**, 430), however, prepared a "polyhalide" CsI_2ICN in aqueous solution from caesium iodide and cyanogen iodide. A simultaneous reaction of type (2) must also have occurred because caesium tri-iodide crystallized after the first salt had been separated. Cyanogen chloride behaves as expected, undergoing reaction of type (4) but not of type (2). Polyhalide formation of type (1) was not observed. Results with other halides will be published later.

Hach and Rundle (*J. Amer. Chem. Soc.*, 1951, **73**, 4321) believe that in the penta-iodide NMe_4I_5 two iodine molecules are polarized by an iodide ion. The compounds $\text{NMe}_4\text{Br}_2\text{CNBr}$ and CsI_2ICN may show a similar polarization of the cyanogen halides, although the direction of polarization may give anions of different types:

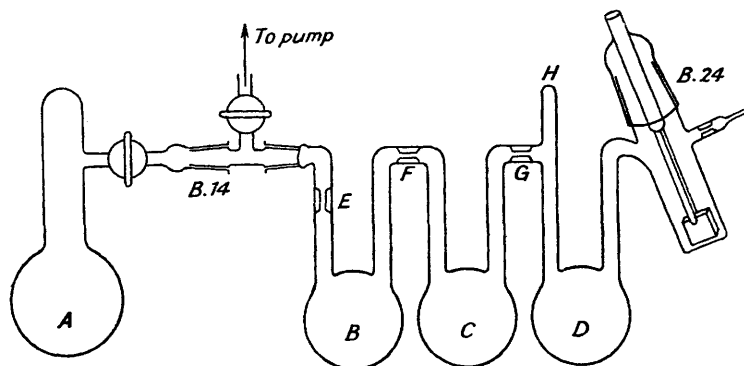


The omission of any reference to cyanogen fluoride is deliberate, for it is doubtful whether it has yet been prepared (Cosslett, *Z. anorg. Chem.*, 1931, **201**, 75; Ruff, *Ber.*, 1936, **69**, 193).

EXPERIMENTAL

Conductivity Measurements.—Cyanogen chloride. The reaction of chlorine with an aqueous solution of potassium zinc cyanide was the most convenient for small-scale preparations of a pure product (Held, *Bull. Soc. chim. Belg.*, 1897, 17, 287; Cook and Robinson, *J.*, 1935, 1011; Klemenc and Wagner, *Z. anorg Chem.*, 1938, 235, 427). Zinc sulphate heptahydrate (66 g.) and potassium cyanide (60 g.), each in 300 ml. of water, were mixed at 0° in a three-necked flask. Chlorine was passed into the vigorously stirred solution through a sintered alundum thimble against a head of water until the initial precipitate almost disappeared (about 3 hr.). The flask

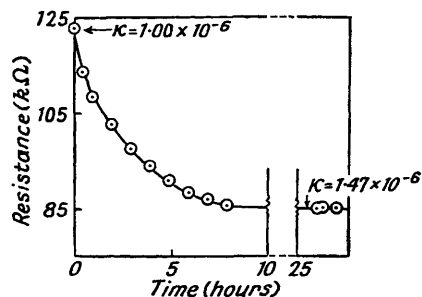
FIG. 1. Conductivity apparatus for cyanogen chloride.



was then connected in series with drying tubes [CaCl_2 , $\text{Mg}(\text{ClO}_4)_2$] and condensers, and the cyanogen chloride removed by heating the flask to 70°. Although the yield is low (60–70%), the product is practically pure and free from chlorine. The cyanogen chloride was purified by refluxing it over mercury and calcium carbonate–magnesium oxide for some hours and collecting a mid-fraction. This fraction was vacuum-distilled into a flask containing phosphoric oxide previously heated at 200° *in vacuo*.

The apparatus shown in Fig. 1 was used for final purification and conductivity measurements. The electrodes of the conductivity cell were lightly platinized, and the cell constant was determined with $n/100$ -potassium chloride solution. The conductivity water used was freshly

FIG. 2. Variation of conductivity of cyanogen chloride with time.



prepared by passage of distilled water through mixed ion-exchange resins. The whole apparatus was thoroughly out-gassed, cyanogen chloride vacuum-distilled from the storage flask *A* to bulb *B*, and the whole sealed at *E*. Cyanogen chloride was then slowly distilled from the solid state into *C*, leaving a residue in *B*. A more volatile fraction was back-distilled from *C* to *B*, and the apparatus sealed at *F*. Similarly, a mid-fraction was collected in *D*, and the apparatus sealed at *G*. When calcium chloride or magnesium perchlorate was used as drying agent the initial conductivities at 0° were about 3×10^{-6} . The result obtained on using phosphoric oxide is given in Fig. 2. The initial conductivity increased from 1.00 to 1.47×10^{-6} . The average temperature coefficient of conductivity $(\Delta\kappa/\Delta T)/\kappa$, determined when the conductivity was constant, was 0.95% between 0° and 10°. Further purification by fractional freezing did not affect these values.

Cyanogen bromide. This was prepared by adding dropwise a solution of sodium cyanide

(85 g.) in water (150 ml.) to bromine (80 ml.) covered with water (50 ml.) during 2 hr. The flask was cooled in ice, and the contents were well stirred. With an apparatus affording efficient recovery of the bromide the yields were over 90%. To purify the bromide it was melted over fused calcium chloride and redistilled at 15 mm.

The conductivity apparatus was similar to that shown in Fig. 1, with the addition of a 60 × 2.5 cm. drying tube, filled with magnesium perchlorate previously dried at 180°. Final dehydration was at 250–251° for 4 hr. *in vacuo*, the water being frozen out in a liquid-air cooled trap at *A*. This trap was removed in a stream of dry nitrogen, and a trap containing freshly distilled cyanogen bromide substituted. The ground joints were fastened with picein wax. The apparatus was evacuated and sealed. The cyanogen bromide was then distilled to and fro between traps *A* and *C*, the drying tube being kept at 50°. Finally, seal *E* was closed, and the solid fractionated from *B* to *C* to *D* with sealing after each transfer. The traps were constructed of thick-walled glass because of the tendency to crack when the condensed cyanogen bromide warmed from liquid-air temperatures. (Thin-walled traps could be used with cyanogen chloride.) The last trap and cell were then placed in a thermostat, and the molten cyanogen bromide poured into the cell. Initial experiments using Pyrex cells with tungsten-wire electrodes gave values

TABLE 5. Variation of conductivity of cyanogen bromide with temperature.

Temp.	60.8°	57.3°	55.6°	55.2°	53.9°	52.4°
$\kappa \times 10^5$ (mhos)	8.87	8.68	8.45	8.43	8.32	8.18

about 1×10^{-4} at 56° but this type of cell was too erratic for accurate measurement. When platinum electrodes were used in a soft-glass cell without ground joints, the conductivity at 60.8° was initially 6.43×10^{-5} but increased to 8.87×10^{-5} after 43 hr. Since the variation

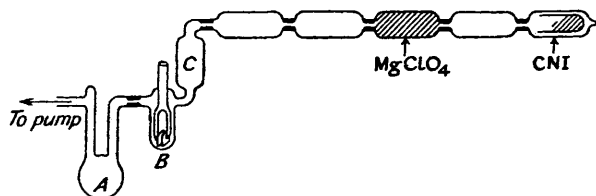


FIG. 3. Conductivity apparatus for cyanogen iodide.

with time was slow after this period, the temperature dependence was determined with allowance for this small decrease of resistance with time. The values are given in Table 5. The linear temperature variation between the m. p. and b. p., $(\Delta\kappa/\Delta T)/\kappa$, was 0.985% on the average. The liquid was non-ohmic but gave no definite decomposition potential, so the figures obtained are not recorded.

Cyanogen iodide. A finely ground mixture of iodine (100 g.) and mercuric cyanide (60 g.; 20% excess) was shaken in a 1-l. conical flask with dry ether (250 ml.) until the liquid became colourless (6 hr.). The solution was filtered, and the ether evaporated. Yields exceeded 90%. The iodide was purified from mercury salts by two sublimations. The final purification was carried out in the apparatus shown in Fig. 3. The cyanogen iodide was sublimed through magnesium perchlorate, dried as described above. Four fractional sublimations brought the iodide into *C*. More volatile fractions collected in the liquid-air-cooled trap *A*, and less volatile fractions were sealed off after each transfer. The sublimation temperature was not allowed to exceed 60°. The platinum electrodes in *B* were silver-soldered to tungsten seals in Pyrex glass. With care, the silver solder could be kept from running over the platinum. The length of exposed tungsten was no more than 1 mm. *B* and *C* were sealed off as one unit and placed in a thermostat

TABLE 6. Variation of conductivity of cyanogen iodide with time.

$\kappa \times 10^4$	Series I.			Series II.*								
	Time (min.)	8.16	9.17	10.5	0.004	0.044	0.24	1.80	3.38	5.95	7.34	9.17
	5	9	11	0	1	1.5	2	3	4.5	7	9.5	11

* Series II was recorded with same specimen 30 min. later.

at $150^\circ \pm 0.1^\circ$. The results given in Table 6 record the variation of conductivity with time after the cell was placed in the thermostat. It was shown that the small volume of liquid required for the cell (3 ml.) reached temperature equilibrium within $\frac{1}{2}^\circ$ in 3 min., so the variations recorded after this time are not due to temperature changes.

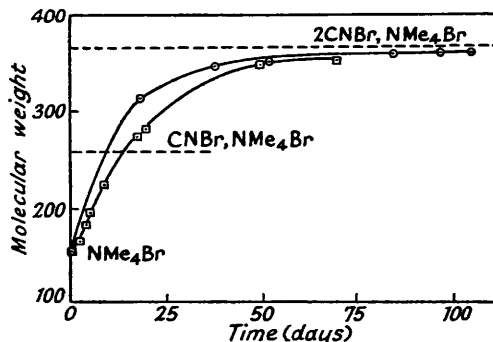
Reactions with Metals.—Cyanogen bromide and the metal were heated in sealed tubes, the bromide was removed *in vacuo*, and the residue examined. Mercury was unaffected after 12 hr.' heating at 120°. With silver there was no apparent attack after one day at 120° but reaction started on heating in a flame. The white residue was extracted with benzene to remove cyanogen bromide and its trimer, and the silver halide or halides formed were extracted with ammonia from unchanged silver. The extract was acidified and boiled with nitric acid. The absence of silver ions in the filtrate showed the absence of silver cyanide. This was confirmed by heating the precipitate, obtained by acidifying the ammonia extract, at 350° to decompose silver cyanide. Again, the absence of silver showed the absence of silver cyanide.

Both aluminium and tin were attacked at 120°, the liquid cyanogen bromide being converted into a hard brown mass of its polymerization and decomposition products. Aqueous extracts, taken after benzene extractions, gave positive tests for bromide ion, showing that some of the metal had been brominated. With these metals there are no stable cyanides as there are for mercury and silver.

Cyanogen iodide and silver were heated in a sealed tube at 170° for 12 hr. The excess of cyanogen iodide was removed *in vacuo* at 60°. Cyanuric iodide is not sufficiently soluble in organic solvents for effective separation, so a partial separation was effected by flotation on water. The heavy silver iodide remained and the suspended matter could be decanted off. The residue was extracted with ammonia to remove the halides, and the absence of silver cyanide shown as above.

The formation of mercuric iodide from mercury could be demonstrated more easily. After

FIG. 4. Combination of cyanogen bromide with tetramethylammonium bromide.



the reaction at 170° only the base of the tube was kept at this temperature. Iodine and cyanogen iodide sublimed to the top of the tube, with a broad band of red mercuric iodide below. This band became yellow when heated at 130°, which is just above the transition point of the mercuric iodide. The absence of mercuric cyanide in the iodide was shown by the fact that thermal decomposition in a sealed tube failed to produce metallic mercury or cyanogen.

Reactions with Halides.—Cyanogen chloride. Potassium, ammonium, and tetramethylammonium chloride were insoluble in cyanogen chloride, and after removal of the latter at 30 cm. were recovered unchanged. Solid tetramethylammonium chloride, exposed to gaseous cyanogen chloride at slightly less than atmospheric pressure, failed to absorb any gas during 2 months.

Cyanogen bromide. The halides were placed in test-tubes which fitted into boiling-tubes containing a 5–10-fold excess of cyanogen bromide mixed with magnesium perchlorate.

Potassium cyanide. The solid blackened, owing to formation of paracyanogen, but the reaction was very slow. Only 0.06 mol. of cyanogen bromide was absorbed after 3 months.

Potassium bromide. Negligible amounts of cyanogen bromide were absorbed after 3 months. Direct analysis by an acid thiosulphate titration (Kurtenacker, *Z. anorg. Chem.*, 1921, **116**, 243) showed an absorption of 0.1%.

Tetramethylammonium bromide. The bromide was dissolved in liquid cyanogen bromide in a sealed tube and, after cooling, the excess of cyanogen bromide was removed *in vacuo*. The residue contained only 53.4% of bromine, far less than for a 1 : 1 compound (Calc. for NMe₄Br : Br, 52.0. Calc. for CNBr : Br, 75.5%). Reaction in alcoholic solution was no more effective. Alcohol was removed by storage over silica gel until crystallisation had occurred. Analysis of the crystals showed that negligible amounts of cyanogen bromide were retained.

The gas–solid reaction, however, produced the compound NMe₄Br, 2CNBr (Found : Br,

64.9; CNBr, 57.1%; equiv., 364. $C_6H_{12}N_3Br_3$ requires Br, 65.5; CNBr, 57.9%; equiv., 366). The results of two such experiments are plotted in Fig. 4, from which the slow approach to the 1:2 composition can be seen. There is no inflection at the 1:1 stage. The bromine was determined by dissolving the substance in dilute nitric acid containing some sulphurous acid, and precipitation as silver bromide after removal of hydrogen cyanide. The cyanogen bromide content was found by its removal *in vacuo*. The residue contained 51.7% of bromine.

Cyanogen iodide. Potassium iodide. Iodine was slowly liberated from potassium iodide by cyanogen iodide vapour at room temperature. After 80 days a 1-g. specimen increased in weight by 9 mg. If the cyanogen iodide had liberated iodine quantitatively the amount expected would be 15 mg. Only 2 mg. of iodine were found by dissolving the residue in water and quickly matching the colour with a similar potassium iodide solution and standard iodine. Thus, in agreement with Mathewson and Wells's work (*loc. cit.*) in aqueous solution, simultaneous liberation of iodine and absorption of cyanogen iodide occurred. The reaction in alcoholic solution is similar: a limited but immediate liberation of iodine occurs on mixing of the initially colourless component solutions.

Tetramethylammonium iodide. A similar iodine liberation occurred which reached 38% of the maximum.

Potassium cyanide. The vapour of cyanogen iodide quickly blackened the cyanide. The weight increase on 1 g. was 9 mg. after 2 months, and the cyanogen content found by the Liebig-Denigès method after sulphurous acid reduction was 35.8%. If paracyanogen is formed it will not be included in this determination of cyanide. The addition of 8 mg. of cyanogen iodide and consequent conversion of 3.1 mg. of cyanogen into paracyanogen gives a calculated cyanogen content of 36.2% (Calc. for KCN: CN, 40.0. Calc. for ICN: CN, 16.5%). Thus the reaction is not an addition, but a conversion into paracyanogen.

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