307. *The Reactions between Hydrogen Iodide and the Cyanogen Halides.*

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The present paper deals with the reactions between hydrogen iodide and cyanogen chloride, bromide, and iodide :

$$2HI + ClCN \longrightarrow HCl + HCN + I_2 + 20 \text{ kg.-cal.} \quad (1)$$
$$2HI + BrCN \longrightarrow HBr + HCN + I_2 + 21 \text{ kg.-cal.} \quad (2)$$
$$HI + ICN \longrightarrow HCN + I_2 + 12 \text{ kg.-cal.} \quad (3)$$

Like the reactions of the preceding paper, reactions (1) and (2) probably go in two stages, *viz.*,

$$HI + ClCN \longrightarrow HCl + ICN + 8 \text{ kg.-cal.} \quad (4)$$
$$HI + BrCN \longrightarrow HBr + ICN + 9 \text{ kg.-cal.} \quad (5)$$

followed by (3). There is also the possibility of intermediate formation of iodine monochloride and monobromide :

$$HI + ClCN \longrightarrow HCN + ICl + 0 \text{ kg.-cal.} \qquad (6)$$

followed by $$HI + ICl \longrightarrow HCl + I_2 + 20 \text{ kg.-cal.} \qquad (7)$$

and $$HI + BrCN \longrightarrow HCN + IBr + 10{\cdot}5 \text{ kg.-cal.} \qquad (8)$$

followed by $$HI + IBr \longrightarrow HBr + I_2 + 10{\cdot}5 \text{ kg.-cal.} \qquad (9)$$

The heats of reaction in equations (1)—(9) are based on the following heats of dissociation: HCN, 97 kg.-cal. (Badger and Binder, *Physical Rev.*, 1931, **37**, 800); ClCN, 75; ICN, 52 (Badger and Woo, *J. Amer. Chem. Soc.*, 1931, **53**, 2572); BrCN, 59 (from the heat of dissociation of the C–Br linkage in aliphatic compounds; Eucken, " Lehrbuch der chemischen Physik," p. 882).

The reactions have been studied in solution in carbon tetrachloride. The free iodine which is formed in every case allows the reactions to be followed colorimetrically. Hydrogen iodide and cyanogen iodide were found to react almost as rapidly as hydrogen iodide and the halogens, the reaction going to half completion in 0·02 second with concentrations 0·001 molar. Cyanogen bromide and cyanogen chloride are less reactive, the time for half reaction in dry solutions being of the order of minutes and hours respectively. Reaction (1) has also been followed manometrically in the gas phase. The reaction between cyanogen and hydrogen iodide has not been studied in detail, but it proceeds at approximately the same rate as (1).

Reactions in Solution.—(a) *Cyanogen iodide.* Solutions of hydrogen iodide were made by passing the gas (prepared by dropping concentrated hydriodic acid on phosphoric oxide in a round-bottomed wash-bottle) through a tube packed with phosphoric oxide and then into a wash-bottle filled with sulphur-free carbon tetrachloride. The saturated solution was diluted, and stored in contact with phosphoric oxide. The iodine which gradually formed by oxidation of hydrogen iodide was removed by means of mercury or silver foil, and the solutions were titrated with sodium hydroxide before dilution to the concentrations required for the experiments. Cyanogen iodide was obtained from laboratory stock, and was recrystallised from carbon tetrachloride after removal of iodine with mercury. Solutions approx. $M/100$ of cyanogen iodide in carbon tetrachloride were made up from a weighed amount of cyanogen iodide and diluted to the required concentrations. The decomposition of cyanogen iodide according to the balanced equation $2ICN \rightleftharpoons C_2N_2 + I_2$ was not fast enough to be troublesome.

Preliminary experiments, in which the solutions of hydrogen iodide and cyanogen iodide were mixed in test-tubes, gave instantaneous reaction. In order to eliminate any effects due to moisture the experiment was repeated with solutions (approx. 10^{-3} M) which had been dried by standing for 2 hours in contact with phosphoric oxide. The dry solutions were rapidly mixed by shaking a thin glass bulb containing hydrogen iodide solution and phosphoric oxide in an outer tube containing cyanogen iodide solution and phosphoric oxide (see Fig. 2 in the preceding paper). No delay in the appearance of iodine colour was observed. The rapid reaction between hydrogen iodide and cyanogen iodide is therefore independent of the presence of water molecules. Although very fast, it is, however, definitely slower than the reactions between hydrogen iodide and the halogens. This was shown by measurements at room temperature with the capillary apparatus illustrated in Fig. 1 of the preceding paper. The reaction with cyanogen iodide, unlike the reactions with the halogens, proved slow enough to be measurable with this apparatus. The measurements were made in the following way. The rate of flow of the mixed liquid along the capillary E was found to be 53 cm. per second. One cm. of E corresponded therefore to $1{\cdot}9 \times 10^{-2}$ second. The relative volumes of hydrogen iodide solution, cyanogen iodide solution, and pure carbon tetrachloride (from bulb B′) flowing into the capillary were determined by filling bulbs A′ and C′ successively with iodine solution of known concentration (B′ and C′, or B′ and A′ being filled with the pure solvent) and titrating the mixed liquid after it had passed through the reaction tube. The concentrations of hydrogen iodide and cyanogen iodide before they entered the capillary being known, it was thus possible to calculate the concentrations in the mixed liquid at the beginning of the reaction. For several different initial concentrations of hydrogen iodide and cyanogen iodide, observations were made of the distance between the point of mixing and the point along the capillary at which the depth of iodine colour was that corresponding to half-reaction. This distance, multiplied by the factor $1{\cdot}9 \times 10^{-2}$, gave τ, the time of half-reaction in seconds. The distance of half-colour was determined by comparison with an iodine solution of the corresponding concentration contained in a capillary of the same glass and dimensions as the reaction tube and mounted alongside it.

The results are in Table I. The first two columns give the initial concentrations of hydrogen iodide and cyanogen iodide in the mixed solutions. Column 3 gives the corresponding value of τ. In column 4 are given values of the velocity constant k, calculated from τ on the assumption that the reaction is bimolecular, and that the rate is given by the equation $d[I_2]/dt = k[HI][ICN]$. The relation between k and τ is then $k = \frac{1}{\tau(a-b)} . \ln(2a-b)/a$, where a is the greater and b the lesser of the concentrations [HI] and [ICN]. It was not possible to work with a very large range of initial concentrations, because at high concentrations τ was less than the time of mixing, and at low concentrations it became difficult to make accurate colour comparisons with the small thickness of liquid in the reaction tube (2 mm.). The somewhat large deviations of k from the mean value $1{\cdot}6 \times 10^4$ are probably within the experimental error, when allowance is made for the difficulty of estimating the half-colour distance, and for the error due to neglecting the time of mixing.

TABLE I.

Reaction $HI + ICN \longrightarrow HCN + I_2$ *in* CCl_4 *Solution at Room Temperature.*

[HI], g.-mol./litre.	[ICN], g.-mol./litre.	$\tau . 10^2$ sec.	$k . 10^{-4}$.
0·0006	0·0017	2·3	2·1
0·0006	0·0008	4·2	2·5
0·0012	0·0008	2·9	2·6
0·0012	0·0004	3·8	1·7
0·0006	0·0004	16·1	0·7
0·0057	0·0002	2·9	0·4
0·0011	0·0002	5·2	1·3
0·0016	0·0002	13·3	1·0
0·0006	0·0008	6·6	1·7
0·0006	0·0004	8·5	1·7
		Mean $k = 1{\cdot}6 \times 10^4$	

(b) *Cyanogen bromide.* Solutions of cyanogen bromide in carbon tetrachloride were made up from a stock of large well-formed crystals which had been prepared for absorption spectrum work. The concentration was determined by adding excess of hydrogen iodide and estimating the liberated iodine colorimetrically.

When solutions of hydrogen iodide and cyanogen bromide were mixed in an open test-tube at room temperature, there was rapid development of iodine coloration. The reaction was not, however, instantaneous, as the reaction between hydrogen iodide and cyanogen iodide appeared to be under similar conditions. With concentrations approximately $M/200$, the development of iodine colour corresponding to half-reaction required about 30 seconds. This does not represent the true velocity of the reaction between hydrogen iodine and cyanogen bromide molecules, because the rate could be slowed down very much by drying the solutions with phosphoric oxide and excluding moist air from the reaction vessel. The catalytic effect of moisture was shown very clearly by an experiment in a reaction vessel divided into two compartments by a thin glass partition which could be smashed by means of a weighted glass hammer. Each compartment was connected by a side tube to bulbs which contained phosphoric oxide and hydrogen iodide or cyanogen bromide solution. The solutions were distilled in a vacuum into the two compartments of the reaction vessel, and the side tubes were then sealed off. When the solutions were mixed by breaking the partition, the glass cracked round the seal, with the result that moist air slowly leaked into the evacuated apparatus. For a few seconds after mixing, the liquid remained colourless, and then a rapid development of colour was observed in the top layer, which was in contact with the moist air that had leaked in.

Some measurements were made of the rate of reaction in dry solutions. Known volumes of the two solutions were shaken with phosphoric oxide in stoppered test-tubes. The dry solutions were rapidly mixed in one test-tube, which was quickly restoppered and shaken vigorously, so that the oxide could remove any moisture introduced during the mixing operation. The progress of the reaction was followed colorimetrically by comparison with iodine solutions in test-tubes similar to that containing the reaction mixture. Under these conditions the time required for half-reaction was about 10 minutes, as compared with 30 seconds for the reaction in open tubes. The reactions were too rapid to allow of accurate colour comparisons being made in the early stages. The usual procedure was to note the time τ required for the solution to develop the colour corresponding to half-reaction. The values of τ were not very reproducible, perhaps owing to differences in the efficiency of drying the solutions. In Table II are tabulated values of τ for different initial concentrations of hydrogen iodide and cyanogen bromide. The tabulated values are the mean of 2 or 3 separate experiments. Bimolecular velocity constants k were calculated on the assumption that the rate is determined by the comparatively slow

TABLE II.

Reaction $2HI + BrCN \longrightarrow HBr + HCN + I_2$ *in* CCl_4 *at Room Temperature.*

[HI], g.-mol./litre	0·0350	0·0050	0·0050	0·0050	0·0025
[BrCN], g.-mol./litre	0·0003	0·0025	0·0013	0·0006	0·0025
τ sec.	160	490	850	1380	1230
k	0·13	0·41	0·20	0·11	0·13
					(mean) 0·2

reaction $HI + BrCN \longrightarrow HBr + ICN$, and that this is followed by the rapid reaction $HI + ICN \longrightarrow HCN + I_2$. If a and b are the initial concentrations of hydrogen iodide and cyanogen bromide, and x the concentration of iodine at time t, then $k = \frac{1}{t(a - 2b)} \ln \frac{b(a - 2x)}{a(b - x)}$. To calculate k from τ, t is put equal to τ and $x = b/2$ or $a/4$ according as a is greater or less than $2b$. In the special case $a = 2b$, $k = 1/a\tau$. The mean value of k is seen from the table to be 0·2 at room temperature, or about 10^5 times smaller than the velocity constant of the reaction between hydrogen iodide and cyanogen iodide.

(c) *Cyanogen chloride.* The cyanogen chloride used was again part of a sample prepared for absorption spectrum measurements. Solutions were made up by distilling a quantity of the chloride into a wash-bottle containing carbon tetrachloride. The concentration of the solutions was determined by adding excess of $N/100$-sodium hydroxide and titrating back with $N/100$-sulphuric acid (Maugin and Simon, *Compt. rend.*, **1919**, **169**, 385).

Experiments in open test-tubes showed that cyanogen chloride was less reactive than the bromide towards hydrogen iodide, the time for half-reaction being a few hours. As in the case of cyanogen bromide, the rate was slowed down by using dry solutions. Experiments were carried out in blackened Jena bottles, the solutions being in contact with phosphoric oxide during the reaction. At suitable intervals 5 c.c. of solution were transferred to stoppered test-tubes, and the iodine content estimated colorimetrically. The results obtained with several different initial concentrations of hydrogen iodide and cyanogen chloride are shown graphically in Figs. 1*a* and 1*b*. Although the rate increases with the concentration of hydrogen iodide and of cyanogen chloride, the reaction does not obey a bimolecular law. Calculated constants, which lie for both temperatures in the range 10^{-3} to 10^{-2}, tend to increase during a run, and dilute solutions give higher constants than concentrated solutions.

FIG. 1*a*.

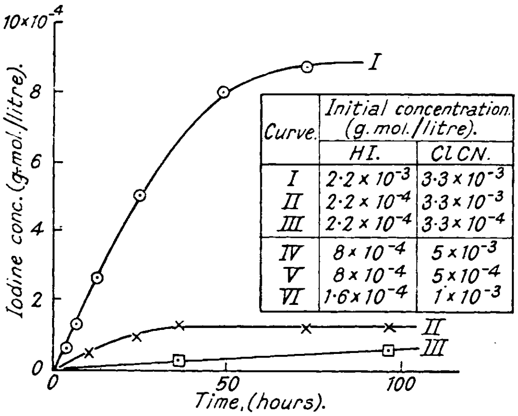


FIG. 1*b*.

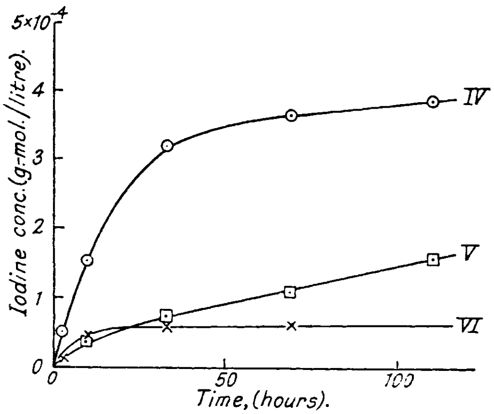


FIG. 1*a*.—*Hydrogen iodide and cyanogen chloride in carbon tetrachloride at* 14°.
FIG. 1*b*.—*Hydrogen iodide and cyanogen chloride in carbon tetrachloride at* 25°.

Reaction in the Gas Phase.—The experiments with solutions indicated that the reactions of hydrogen iodide with cyanogen iodide and bromide were too rapid to be followed manometrically in the gas phase. The slower reaction with cyanogen chloride was therefore selected for investigation in the apparatus shown in Fig. 2. The glass spring gauge A, used as a null instrument, measured pressures to ± 0·1 mm. The reaction vessel B (volume 150 c.c.) could be shut off from the gas storage systems and pumps by the ungreased ground joint D, the male part of which was weighted with mercury and could be raised or lowered by means of a platinum wire suspension. A and B were immersed in a water-filled Dewar vessel, which was fitted with a small heating coil and stirred by bubbles of compressed air. The side tube C (volume 3 c.c.) could be cooled to any required temperature to condense out iodine. It was usually kept at room temperature. Connexion was made to the pumps and gas reservoirs by the ground joints E and F, which allowed the reaction vessel to be dismounted and cleaned when necessary.

Cyanogen chloride, distilled from phosphoric oxide, was stored at room temperature as a liquid. Hydrogen iodide was freed from moisture and phosphonium iodide, and stored in a blackened reservoir. The reaction was studied at temperatures 14° and 25°, with partial pressures of the reactants between 15 and 120 mm. The decrease of pressure obtained when the reaction was allowed to go to completion was approximately three times as much as would be expected from the reaction $2HI + ClCN \longrightarrow HCl + HCN + I_2$ (cryst.). The solid deposit, which appeared in A and B as well as in C, was light brown and quite unlike a deposit of iodine. This deposit lowered the efficiency of the valve D after a few runs had been made. It could not be removed from the glass by evacuation with a mercury diffusion pump. It was insoluble in light petroleum or carbon tetrachloride, but readily soluble in water or alcohol. These properties suggest that the deposit is formimide chloride, CH_2NCl, produced by interaction of hydrogen chloride and hydrogen cyanide. The magnitude of the pressure change is therefore accounted for by the reaction $2HI + ClCN \longrightarrow CH_2NCl + I_2$ (cryst.).

FIG. 2.

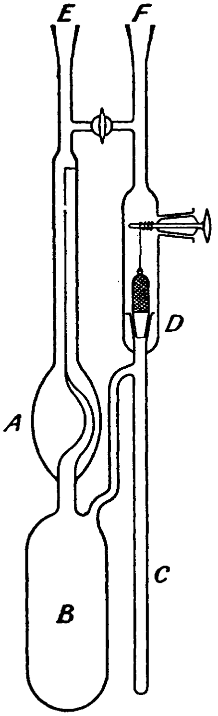
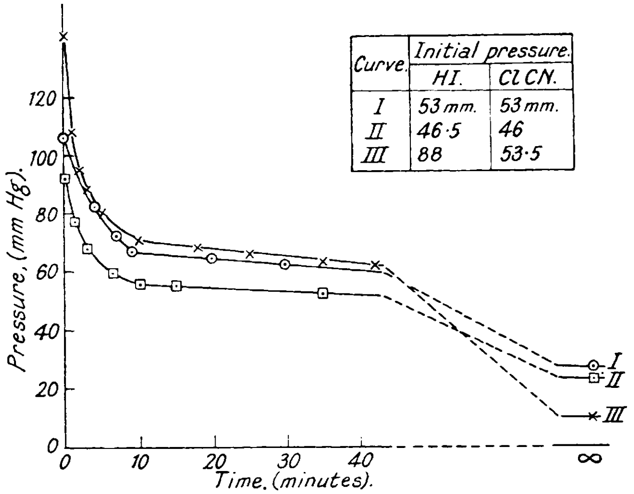


FIG. 3.

Hydrogen iodide and cyanogen chloride in gas phase at 25°.



The course of the reaction at 25° is shown in Fig. 3. The curves show a rapid initial pressure decrease, followed by a much slower linear portion. The marked " break " in the curves cannot be explained by assuming that the reaction $HCl + HCN \longrightarrow CH_2NCl$ is much slower than $2HI + ClCN \longrightarrow HCl + HCN + I_2$, as this would require the break to occur earlier than is observed. It is more likely that the production of formimide iodide, CH_2NI, and consequent removal of hydrogen iodide from the gas phase, is the cause of the slowing-down. The final linear part of the curves would then correspond to slow interaction of cyanogen chloride with the " bound " hydrogen iodide in the surface deposit. Velocity constants calculated from the initial reaction rates were of the order 10^{-5} at 14° and 10^{-5} at 25°, but varied too much to allow an estimate of the temperature coefficient.

At 14° the gas reaction was roughly 20 times, and at 25° 100 times, as fast as in solution in carbon tetrachloride at comparable concentrations. The bimolecular constants for solutions did not show the falling-off characteristic of the gas reaction, but rather an increase. This is probably connected with the presence of the large surface of not absolutely dry phosphoric oxide. Water decomposes formimide iodide and would prevent the locking-up of hydrogen iodide which we believe to explain the peculiarities of the gas reaction.

Heats of Activation.—If the reactions described above are homogeneous and proceed at rates governed by binary collisions between hydrogen iodide and cyanogen halide, the energy of activation of the rate-determining reactions (3), (4), and (5), or possibly (3), (6), and (8) can be calculated from the collision efficiencies. This leads to values 9, 15, and 18 kg.-cal. for the reactions of hydrogen iodide with cyanogen iodide, bromide, and chloride respectively. These values are lower limits in the case of the bromide and the chloride, since part of the observed velocity may be due to surface reaction. Consideration of diffusion rates shows, however, that the reaction with cyanogen iodide is too fast to be appreciably influenced in this way. The reactivity towards hydrogen iodide decreases in the order Cl_2, ICN, BrCN, ClCN. This is the same as the order which Polanyi and his collaborators find for the reaction with sodium atoms (Cosslett, *Z. anorg. Chem.*, 1931, **201**, 75).

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