306. *The Reaction between Hydrogen Iodide and Chlorine.*

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HYDROGEN iodide reacts readily with chlorine, giving hydrogen chloride and iodine. Iodine monochloride, which also reacts rapidly with hydrogen iodide, is probably formed as an intermediate :

$$HI + Cl_2 \longrightarrow HCl + ICl + 21 \text{ kg.-cal.} \qquad (1)$$

$$HI + ICl \longrightarrow HCl + I_2 + 20 \text{ kg.-cal.} \qquad (2)$$

The rate of reaction corresponds to heats of activation E less than 5·5 kg.-cal. for (1) and (2). Recent theoretical work would appear to require considerably higher values of E for homogeneous bimolecular reactions of this type (London, *Z. Elektrochem.*, 1929, **35**, 552; Eyring, *J. Amer. Chem. Soc.*, 1931, **53**, 2537). In particular, from considerations of nuclear separation and collision diameters, reactions (1) and (2) would be expected to have greater heats of activation than the reaction $I_2 + Cl_2 \longrightarrow 2ICl$ (Franck and Rabinowitsch, *Z. Elektrochem.*, 1930, **36**, 794). The latter has, however, $E > 15$ kg.-cal., which means that (1) and (2) are at least 10^6 times faster than theory predicts.

Reaction in the Gas Phase.—Austen, and Longinescu and Theodosiu state that a flame is produced when a jet of chlorine is introduced into hydrogen iodide (*Amer. Chem. J.*, 1889, **11**, 270; *Bul. Soc. Româna Stiin.*, **1923**, **26**, 19). We have confirmed this, but believe the initiation of flame to depend on the presence of red phosphorus or phosphonium iodide. When we prepared hydrogen iodide from phosphoric oxide and concentrated hydriodic acid, and removed phosphonium iodide by passage through a trap at − 30°, no flame was produced, but there was always instantaneous formation of iodine vapour. Unsuccessful attempts were made to start the flame in pure hydrogen iodide by means of charcoal and manganese dioxide catalysts, which are effective in initiating the chlorine–hydrogen sulphide flame (Ludlam and Ritchie, unpublished work). Silica gel was also without effect, but we succeeded in starting the flame with a trace of red phosphorus, which burns in chlorine.

Some experiments were carried out in which jets of chlorine and hydrogen iodide reacted in the absence of any surface. In a preliminary experiment in a fume chamber, the colour of iodine was immediately produced where the gas streams crossed. In the second experiment we used a 250 c.c. bulb through which dry nitrogen was rapidly passed. Two jets were sealed into the bulb, one being mounted eccentrically on a ground joint so that its position could be adjusted. The chlorine and hydrogen iodide were stored at − 78° in wash-bottles, and carried over phosphoric oxide to the jets in a stream of nitrogen. It was evident from the precipitation of small iodine crystals in the gas phase that the reaction proceeded in the body of the gas. There was much turbulence in the bulb, and the iodine which was blown between the jets and the walls made it impossible to see where the reaction started. In a third experiment a 12-litre tin box served as reaction vessel. A thick layer of phosphoric oxide was spread over the bottom, and jets for dry air, hydrogen iodide, and chlorine passed through the sides. The gases were pumped away through a fourth tube. The reaction was observed through a glass window waxed on to the lid. Although some difficulty was found in starting the gas streams simultaneously, in favourable cases the development of iodine coloration could clearly be seen to start at the junction of the hydrogen iodide and chlorine streams, more than 3 cm. from the nearest solid surface.

Reaction in Solution in Inert Solvents.—When solutions of hydrogen iodide and chlorine in carbon tetrachloride are mixed, the appearance of iodine coloration is instantaneous. If chlorine is in excess, this rapid reaction is followed by slow formation of iodine mono- or tri-chloride. In order to measure the velocity of the rapid reaction, the apparatus shown in Fig. 1*a* was constructed. A and B are wash-bottles in which solutions of hydrogen iodide and chlorine in sulphur-free carbon tetrachloride are stored over phosphoric oxide. In C the pure solvent is similarly stored. Liquid from the wash-bottles can be sucked up into the 250 c.c. bulbs A′, B′, C′. By opening tap D to the atmosphere the solutions can be forced to mix at M. Pure carbon tetrachloride flows down the central capillary E (Fig. 1*b*) while the solutions flow through F and G, which can be connected to or shut off from A′ and B′ by rotating the ground joint at M. This joint, like all the taps, is ungreased. When wet with carbon tetrachloride it is quite transparent, and the change of colour of the liquid flowing down the capillary E can be followed from the point of mixing. F and G (1 mm. diam.) are bored tangential to E (2 mm. diam.) in order to promote rapid mixing (compare Hartridge and Roughton, *Proc. Roy. Soc.*, 1923, *A*, **104**, 376). Tap H controls the proportion of pure solvent and solutions flowing into E.

Most of our experiments with this apparatus were made with the liquid flowing through E at a velocity of 120 cm. per sec. Under these conditions, with initial concentrations of hydrogen iodide and chlorine in the mixed solutions varying from 0·05*M* to 0·0005*M*, the reaction was half complete in about 1 cm. (0·0085 sec.). Experiments with iodine solution in A′ and carbon tetrachloride in B′ and C′ showed that this apparent delay represents the time required for the solutions to mix. The value 0·0085 second is therefore an upper limit only for the time of half-reaction. When iodine monochloride was substituted for chlorine in B, the same value was obtained. These results allow an upper limit to be calculated for the energy of activation of reactions (1) and (2). The collision frequency for the dissolved molecules being assumed the same as in the gas phase, the collision efficiency is found to be $> 2{\cdot}6 \times 10^{-6}$ at room temperature. E is therefore $< 7{\cdot}6$ kg.-cal.

The reaction is too fast to be accounted for by the mechanism $2HI + Cl_2 \longrightarrow 2HCl + I_2$. With 0·0005*M* solutions the calculated time for half-reaction would be 0·01—0·1 second, assuming that every ternary collision $2HI + Cl_2$ led to reaction. This compares with the observed time of $< 0{\cdot}01$ second. The iodine colour which developed with more dilute solutions was too faint to allow the capillary apparatus to be used. Test-tube experiments in which dry solutions of hydrogen iodide and chlorine ($10^{-4}M$ and $5 \times 10^{-5}M$ respectively) were employed gave reaction in less than 0·2 second, against a calculated time 2—20 seconds. The uncertainty in calculated times arises from the uncertainty in the ratio ternary/binary collisions (taken as

10^{-3} to 10^{-4} at atmospheric pressure). The number of ternary collisions is barely sufficient to maintain the observed rate, even if there is no orientation factor to limit the number of fruitful collisions, and zero heat of activation. Both of these conditions are most improbable in a reaction involving the breaking of three bonds and the formation of three others. During the observed reaction time, the molecules of hydrogen iodide and chlorine could diffuse a distance of a few hundredths of a mm. only through the solvent. Reaction at the glass surfaces is therefore out of the question.

Reaction between Dry Solutions in Sealed Tubes.—In order to make sure that the rapid reaction described above was not dependent on the presence of traces of moisture, solutions of hydrogen iodide and chlorine in carbon tetrachloride (approx. $10^{-4}M$) were distilled through a packed column of phosphoric oxide in an evacuated all-glass apparatus into tubes of the type shown in Fig. 2. The solutions were mixed by breaking the thin end of the inner tube. In another series of experiments the solutions were sealed off in contact with phosphoric oxide, kept for some hours, and mixed as before. Immediate appearance of iodine was always observed. Thus there is no possibility of accounting for the low heat of activation by an ionic mechanism $I' + Cl_2 \longrightarrow ICl + Cl'$.

FIG. 1*a*.

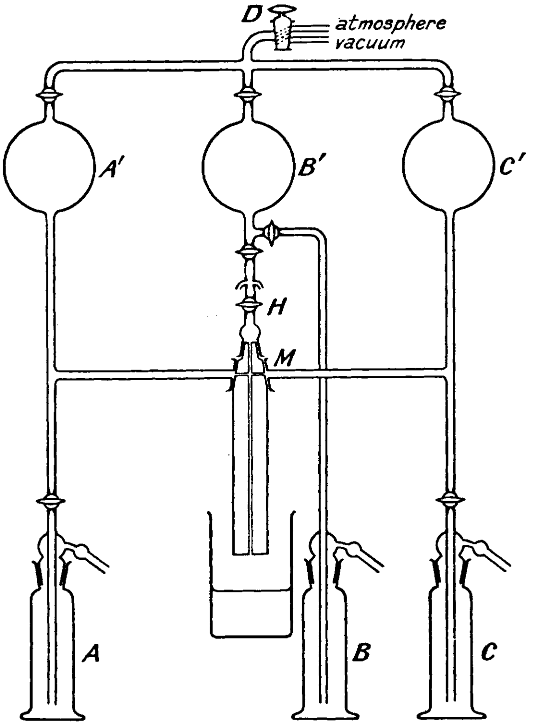


FIG. 1*b*.

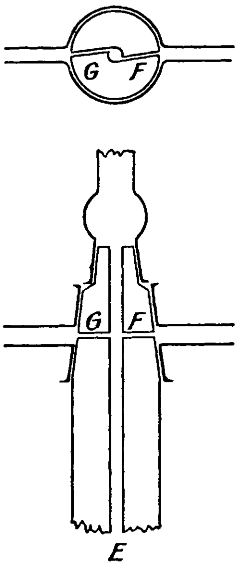
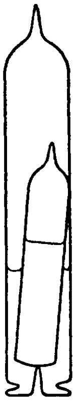


FIG. 2.



The above experiments were all carried out at room temperature. The reaction has also been studied in solutions cooled with carbon dioxide snow or pentane + liquid air. Hexane and *iso*pentane were used as solvents instead of carbon tetrachloride because of their lower freezing points. After the solutions had been distilled through phosphoric oxide as before, the tubes were sealed off and cooled to − 78° (solvent hexane) or − 110° (solvent *iso*pentane). When the solutions were mixed, immediate reaction was always observed. The time required for half-reaction was certainly less than 0·2 second. This leads to a value $E < 5{\cdot}5$ kg.-cal. as an upper limit for the heat of activation of the bimolecular reactions (1) and (2).

The experiments at low temperatures show that the high reaction rate is not maintained by a chain mechanism in which the initial step requires considerable activation energy: *e.g.*, the reaction might be imagined to proceed by a chain of ternary collisions involving chlorine atoms: $Cl + HI + Cl_2 \longrightarrow ClH + ICl + Cl$. All homogeneous reactions, however, leading to the production of chlorine atoms from the system HI + Cl_2 require more than 9 kg.-cal. activation, and could not supply sufficient chlorine to give the observed velocity at − 110°.

That the initiation of such chains at a surface (as in the reaction of Alyea and Haber, *Z. physikal. Chem.*, 1930, **10**, 193) can in this case be neglected, follows from the experiments with gaseous hydrogen iodide and chlorine in the absence of walls.

DISCUSSION.

It is concluded from the above experiments that the reaction of chlorine with hydrogen iodide is homogeneous and bimolecular, proceeding in the two stages $HI + Cl_2 \longrightarrow HCl + ICl$; $HI + ICl \longrightarrow HCl + I_2$. Both stages have heats of activation less than 5·5 kg.-cal.

Two alternative mechanisms are, however, not excluded by these experiments, and may be responsible for the low value of E. Ternary collisions of the type $HI + Cl_2 + M$ (M any molecule) could lead to HCl + ICl either directly or by way of an intermediate addition compound $HICl_2$. Our measurements of the reaction in solution do not exclude a mechanism involving this kind of ternary collision, owing to the large concentration of solvent molecules. The work of Jost (*Z. physikal. Chem.*, 1931, **14**, 413) on the analogous reaction between hydrogen bromide and chlorine at low pressures shows that such a mechanism would require a very low heat of activation ($<$ 2 kg.-cal. for $HBr + Cl_2$) to account for the observed rate. Jost regarded as improbable such a low value of E, and hence preferred the bimolecular mechanism, for which he gives $E < 9$ kg.-cal. The theoretical objection to a low value of E is, however, not so strong for a ternary mechanism, and the question must be left to be decided by experiments at lower pressures than those Jost used.

The formation in binary collisions of an unquantised molecule $HICl_2$, and its subsequent breakdown to HCl + ICl, would be expected to require the same activation as the reaction leading directly to HCl + ICl. The production of such an addition compound, not necessarily stable, is essentially the step requiring activation in a bimolecular exchange reaction according to London's theory. It cannot therefore account for the abnormally low activation of reactions (1) and (2).

When chlorine burns in hydrogen iodide with the production of flame, the mechanism is probably quite different from that of the normal reaction which we have been discussing. Once a flame is started, the hydrogen iodide in the immediate neighbourhood will be largely dissociated into hydrogen and iodine, and what is observed may be the well-known flame of chlorine burning in hydrogen.

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