

H₂ – Y₂ Reactions (Y = Cl, Br, I): A Comparative and Mechanistic Aspect

Suresh Kumar Sharma*

Department of Chemistry, D. A. V. College, Abohar – 152116, Punjab, India

*E-mail: suresh30091978@gmail.com

Abstract The reaction between hydrogen and chlorine shows resemblance to that between hydrogen and bromine but is considerably more complicated, owing to the larger number of elementary processes that play a significant part in it. The reaction scheme proposed for the hydrogen-chlorine reaction differs in several important respects from that for the hydrogen-bromine reaction. The main differences are seen to be (1) the inclusion of the reaction $H + HBr \rightarrow H_2 + Br$ and the exclusion of $H + HCl \rightarrow H_2 + Cl$, and (2) the different chain-terminating steps, $Br + Br \rightarrow Br_2$ being assumed for bromine and the three processes $H + O_2$, $Cl + O_2$, and $Cl + X$ in the chlorine reaction. The rather marked difference between the reactions of chlorine, bromine, and iodine with hydrogen is that the hydrogen-iodine reaction is elementary while the others are not.

Keywords: Reaction, Hydrogen-Chlorine, Hydrogen-Bromine, Hydrogen-Iodine, Chain-terminating

HYDROGEN-BROMINE REACTION

The formation of hydrogen bromide from hydrogen and bromine is a reaction the mechanism of which is well understood. The thermal reaction was first studied by Bodenstein and Lind (1907) over the temperature range from 205 to 302°C, and at pressures of the order of 1 atm. They found empirically that their results could be fitted to the equation

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + [HBr]/m[Br_2]} \quad (1)$$

where k and m are constants, the latter having the value of about 10 and independent of temperature. This equation shows that hydrogen bromide inhibits the reaction, and it was found that iodine exerted an even more powerful inhibition; water, air, and carbon tetrachloride on the other hand had no inhibiting action.

Bodenstein and Lind suggested that the appearance of the bromine as a square root probably indicated that bromine atoms play an important part in

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the reaction; however, the results were not properly explained until 1919, when Christiansen, Herzfeld, and Polyani independently proposed the mechanism



It was found that the use of steady-state treatment give rise to the kinetic law

$$\frac{d[HBr]}{dt} = \frac{2k_2(2k_1/k_5)^{1/2}[H_2][Br_2]^{1/2}}{1 + k_4[HBr]/k_3[Br_2]} \quad (2)$$

This is of the same form as the empirical equation (1), with

$$k = 2k_2(2k_1/k_5)^{1/2} \quad (3)$$

and

$$m = k_3/k_4 \quad (4)$$

The individual rate constants k_1 to k_5 for the elementary reactions have all been evaluated, and the methods by which this has been done will now be indicated.

The experimentally determined constant k is equal to $2k_2(2k_1/k_5)^{1/2}$ and the ratio $\left(\frac{k_1}{k_5}\right)$ is the equilibrium constant for the dissociation of bromine into atoms, the value for which has been determined by Bodenstein and Cramer (1916), the rate constant k_2 can therefore be calculated. According to Jost (1929), the best value for it is given by

$$\log k_2 = 12.30 + 0.5 \log T - \frac{17,600}{2.303 RT} \quad (5)$$

The activation energy is thus 17.6 kcal, and since the reaction is endothermic to the extent of 16.4 kcal, it follows that the activation energy for the reverse reaction (iv) is equal to 1.2 kcal.

The value of m , equal to k_3/k_4 , is found experimentally to be independent of the temperature; the two reactions (iii) and (iv) therefore have the same activation energy, so that the activation energy of (iii) is also about 1.2 kcal.

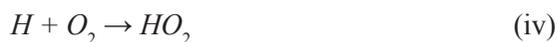
Since the value of k is about 10, reaction (iii) proceeds about 10 times as fast as (iv), in spite of the fact that the activation energies are the same. The difference in rates must be accounted for in terms of frequency factors, that, for (iv) being one-tenth of that for (iii).

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HYDROGEN-CHLORINE REACTION

The reaction between hydrogen and chlorine shows resemblance to that between hydrogen and bromine but is considerably more complicated, owing to the larger number of elementary processes that play a significant part in it. Hydrogen and chlorine reacts thermally at temperatures above 200°C. Both the thermal and photochemical reactions have been the subject of much study, particularly the photochemical reaction, the details of which are now fairly well understood. A striking feature of the photochemical reaction between hydrogen and chlorine is the extremely large quantum yield that is obtained under suitable conditions, values as high as 10⁶ having been reported (Bodenstein, 1913). This is in marked contrast to the situation with hydrogen and bromine, where the quantum yield is usually less than unity. The reason for this difference is that the chain-propagating reactions are more rapid with chlorine than with bromine.

The most satisfactory mechanism would appear to be the following, which was proposed in 1921 by Gohring (1921)



Here X may be any substance which removes chlorine atoms. The effect of oxygen is to contribute to the induction period during which no reaction occurs and to influence markedly the rate of the reaction after it has started. Minute traces of oxygen have a strong effect on the rate.

On the basis of a survey of the experimental work that had been carried out, Thon (1926) proposed that the rate of the reaction could be represented by

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$$\frac{d[HCl]}{dt} = \frac{k[H_2][Cl_2]^2}{[O_2]([H_2] + [Cl_2]/10)} \quad (6)$$

This expression implies an infinite rate in the complete absence of oxygen, and Cremer (1927) pointed out that the expression is obeyed only down to an oxygen pressure of about 0.04 mm. A more accurate expression for the rate, valid down to much lower pressures, was given by Bodenstein and Unger (1930); this is

$$\frac{d[HCl]}{dt} = \frac{k[H_2][Cl_2]^2}{m[Cl_2] + [O_2]([H_2] + [Cl_2]/10)} \quad (7)$$

$$\text{where } k = \frac{2k_3}{k_4} \quad m = \frac{[X]k_3k_6}{k_2k_4} \quad \frac{1}{10} = \frac{k_3k_5}{k_2k_4}$$

At oxygen pressures higher than 0.04 mm the first term in the denominator can be neglected, so that Eq. (7) is obeyed.

INDIVIDUAL RATE CONSTANTS

On the basis of the overall rates of the thermal and photochemical reactions, and from the results of other experiments, conclusions have been reached concerning the individual rate constants and activation energies for some of the elementary processes. The values obtained for the activation energies are summarized in Table 1, which includes also the results for bromine and iodine.

Table 1: Activation Energies for Elementary Processes Occurring in the Hydrogen-Halogen Reactions

Reaction	Activation Energy, kcal, with <i>Y</i> equal to		
	<i>Cl</i>	<i>Br</i>	<i>I</i>
$Y + H_2 \rightarrow HY + H$	6.0	17.2	33.4
$H + Y_2 \rightarrow HY + Y$	2 - 3.6	1.2	0.0
$H + HY \rightarrow H_2 + Y$	5.0	1.2	1.5

The activation energy for the reaction $Cl + H_2 \rightarrow HCl + H$ has been determined directly by Rodebush and Klingelhoefer (1933) by passing atomic chlorine into hydrogen. The activation energy was calculated from the temperature coefficient of the rate of formation of hydrogen chloride and also from the

rate at one temperature, simple collision theory being assumed to apply; the agreement was very good, the activation energy obtained by the two methods being 6.0 kcal. The activation energy of the reverse reaction, $H + HCl \rightarrow H_2 + Cl$, is found from the above value and the heat of the reaction which is 1.0 kcal: the activation energy of the reaction is therefore 5 kcal. The energy of activation for the reaction $H + Cl_2 \rightarrow HCl + Cl$, cannot be arrived at with the same degree of precision. The reaction is so rapid that direct measurement is difficult, and the value must be obtained from an analysis of the overall rate. This gives a value of about 2 kcal (Hertel, 1931; Padoa and Butironi, 1916, 1917; Porter et al., 1926) so that a lower limit of 2 kcal can be assumed for E_3 .

An upper limit for the activation energy may be determined from experimental fact that there is no measurable inhibition of the reaction by hydrogen chloride, in contrast with the situation with the hydrogen-bromine reaction. This implies that the reaction $H + HCl \rightarrow H_2 + Cl$ proceeds at least 100 times as slowly as $H + Cl_2 \rightarrow HCl + Cl$, from which, assuming equal frequency factors, it can be concluded that the activation energies differ by at least 1.4 kcal. Since the activation energy for the former reaction is 5.0 kcal, it follows that for $H + Cl_2 \rightarrow HCl + Cl$, is less than 3.6 kcal. The value must therefore be between 2 and 3.6 kcal.

The rate of chain-ending process $H + O_2$ has also been investigated. The activation energy of the process is certainly very small; it has been seen to be 2 kcal less than that of the reaction $H + Cl_2 \rightarrow HCl + Cl$, the energy for which must be less than 3.6 kcal; consequently the activation energy for $H + O_2$ is not greater than 1.6 kcal. Since this reaction has activation energy of 2 kcal less than that of $H + Cl_2$ it might be expected to proceed about fifty times as fast, but Bodenstein and Schenck (1933) found experimentally that it actually occurs with about one-twentieth the speed. This implies that only 1 collision in 1,000 of the collision with sufficient energy of activation is effective, and this suggests that a third body is necessary; as has been seen, the ratio of trimolecular to bimolecular collisions is, on the basis of collision theory (which is probably applicable to these simple reactions), of the order of 1:1,000.

COMPARISON OF THE HYDROGEN-HALOGEN REACTIONS

The reaction scheme proposed for the hydrogen-chlorine reaction differs in several important respects from that for the hydrogen-bromine reaction. Now that the activation energies are known, the reason for the differences can easily be understood on the basis of Table 1, in which the activation energies are compared. The main differences are seen to be (a) the inclusion of the reaction $H + HBr \rightarrow H_2 + Br$ and the exclusion of $H + HCl \rightarrow H_2 + Cl$, and (b) the

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different chain-terminating steps, $Br + Br \rightarrow Br_2$ being assumed for bromine and the three processes $H + O_2$, $Cl + O_2$, and $Cl + X$ in the chlorine reaction.

The reason for neglecting the reaction $H + HCl \rightarrow H_2 + Cl$ is seen from the activation energies given in Table 1. The reaction will proceed at a negligible speed in comparison with $H + Cl_2 \rightarrow HCl + Cl$, activation energy being 2 to 3 kcal greater; the fact that there is no inhibition by was in fact used to obtain a value for this activation energy difference. In the bromine reaction, on the other hand, $H + Br_2 \rightarrow HBr + Br$ and $H + HBr \rightarrow H_2 + Br$ proceed at comparable speeds, so that the latter reaction is significant, and hydrogen bromide inhibits the reaction.

The reaction $H + O_2$ is significant in the chlorine reaction because its speed is one-twentieth of that of $H + Cl_2$. Since the reaction $H + Br_2$ is appreciably faster than $H + Cl_2$, the activation energy being 1 to 2 kcal less, the $H + O_2$ reaction is negligible compared with $H + Br_2$. The same applies to the other chain-ending processes $Cl + O_2$ and $Cl + X$, which are also probably three-body reactions. On the other hand $Br + Br$ is the only significant chain-ending process in the bromine reaction.

It is clear that the rather marked differences between the reactions chlorine, bromine, and iodine with hydrogen are due to differences between activation energies of elementary processes, and a theoretical treatment of the problem (Wheeler et al., 1936) has contributed toward an understanding of problem in particular, it explains why the hydrogen-iodine reaction is elementary while the others are not. In Table 2 the values of the activation energies of the relevant elementary processes are collected.

Table 2: Calculated Activation Energies of the Hydrogen-Halogen Reactions

Reaction	Activation Energy, kcal, with Y equal to		
	Cl	Br	I
$H_2 + Y_2 \rightarrow 2 HY$	50.0	45.0	40.7
$\frac{1}{2} Y_2 \rightarrow Y$	28.0	23.0	17.0
$Y + H_2 \rightarrow HY + H$	6.0	17.6	33.4
$H + Y_2 \rightarrow HY + Y$	2 - 3.6	1.2	0.0
Sum of three last values	37.0	41.0	50.4

Consider first the reaction between hydrogen and iodine; the experimental value for the activation energy of the molecular reaction is 40.7 kcal. In order for reaction to proceed by a radical mechanism, the initial step would be $\frac{1}{2} I_2 \rightarrow I$, which requires 17 kcal, for the production of 1 mole of iodine atoms,

and this would have to be followed by the third and fourth reactions for the production of 2 moles of hydrogen iodide. The activation energy for the overall process is therefore

$$33 + 17 + 0 = 50 \text{ kcal}$$

and since this is higher than that for the molecular mechanism, the latter will predominate, as is found to be the case.

The situation is otherwise with chlorine and bromine. With chlorine the calculated activation energy for the elementary molecular process is 50 kcal, whereas that for the production of two molecules of hydrogen chloride by the atomic mechanisms is $28 + 6 + 3 = 37$ kcal. The atomic mechanism will therefore predominate; the reaction therefore involves free atoms, and the kinetics are relatively complicated, owing to the number of stages involved. The atomic mechanism also predominates in the hydrogen-bromine reaction, the activation energy being $23 + 18 + 1 = 42$ kcal as compared with 45 kcal for the molecular process.

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