① Hydrogen – Chlorine Reaction (photochemical)

The proposed reaction mechanism is

① $Cl_2 + h\nu \longrightarrow 2Cl^{\cdot}$; $I \rightarrow$ the intensity of light absorbed

② $Cl^{\cdot} + H_2 \xrightarrow{k_2} HCl + H^{\cdot}$

③ $H^{\cdot} + Cl_2 \xrightarrow{k_3} HCl + Cl^{\cdot}$

④ $H^{\cdot} + O_2 \xrightarrow{k_4} HO_2^{\cdot}$

⑤ $Cl^{\cdot} + O_2 \xrightarrow{k_5} ClO_2^{\cdot}$

⑥ $Cl^{\cdot} + X \xrightarrow{k_6} ClX^{\cdot}$

Note: * Here X is any substance that can remove chlorine atoms or radicals.

* The chain-ending step $Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$ is not included in this scheme, since under ordinary conditions $Cl^{\cdot}$ radicals are removed more effectively by reactions ⑤ & ⑥. ~~The reason for this is~~

* The species $HO_2^{\cdot}$ that is formed in reaction ④ is unstable and is converted eventually into water and oxygen (O_2).

As the radicals $Cl^{\cdot}$ and $H^{\cdot}$ are very reactive, both of them are present at very low concentrations in the reaction system. Therefore, the steady-state hypothesis must be applied to $Cl^{\cdot}$ & $H^{\cdot}$.

② The rate of formation of Cl· radicals by reaction ① is 2I, and the steady-state equation for Cl· radicals is

$$\frac{d[Cl\cdot]}{dt} = 2I - k_2[Cl\cdot][H_2] + k_3[H\cdot][Cl_2] - k_5[Cl\cdot][O_2]$$
$$- k_6[Cl\cdot][X] = 0 \quad \text{——— (E1)}$$

The steady-state equation for H· radicals is

$$\frac{d[H\cdot]}{dt} = k_2[Cl\cdot][H_2] - k_3[H\cdot][Cl_2] - k_4[H\cdot][O_2] = 0 \quad \text{——— (E2)}$$

from which (E2) it follows that

$$k_2[Cl\cdot][H_2] = k_3[H\cdot][Cl_2] + k_4[H\cdot][O_2]$$

$$[Cl\cdot] = \frac{k_3[H\cdot][Cl_2] + k_4[H\cdot][O_2]}{k_2[H_2]} \quad \text{——— (E3)}$$

Introduction of (E3) into equation (E1), one obtains

$$2I - k_2[Cl\cdot][H_2] + k_3[H\cdot][Cl_2] - k_5[Cl\cdot][O_2]$$
$$- k_6[Cl\cdot][X] = 0$$

or, $$2I - k_2 \frac{k_3[H\cdot][Cl_2] + k_4[H\cdot][O_2]}{k_2[H_2]}[H_2] + k_3[H\cdot][Cl_2]$$
$$- k_5 \frac{k_3[H\cdot][Cl_2] + k_4[H\cdot][O_2]}{k_2[H_2]}[O_2]$$
$$- k_6 \frac{k_3[H\cdot][Cl_2] + k_4[H\cdot][O_2]}{k_2[H_2]}[X] = 0$$

(3)

$$\text{or, } 2I - k_3[H^\cdot][Cl_2] + k_4[H^\cdot][O_2] + k_3[H^\cdot][Cl_2]$$

$$- \frac{k_5 k_3}{k_2[H_2]}[H^\cdot][Cl_2][O_2] - \frac{k_5 k_4}{k_2[H_2]}[H^\cdot][O_2]^2$$

$$- \frac{k_6 k_3}{k_2[H_2]}[H^\cdot][Cl_2][X] - \frac{k_6 k_4}{k_2[H_2]}[H^\cdot][O_2][X] = 0$$

$$\text{or, } 2I k_2[H_2] = k_2 k_4[H^\cdot][H_2][O_2] \quad \text{small}$$

$$+ k_3 k_5[H^\cdot][Cl_2][O_2] + k_4 k_5[H^\cdot][O_2]^2$$

$$+ k_3 k_6[H^\cdot][Cl_2][X] + k_4 k_6[H^\cdot][O_2][X] = 0$$

Neglecting small term $k_4 k_5[H^\cdot][O_2]^2$, we get

$$[H^\cdot]\{k_2 k_4[O_2][H_2] + k_3 k_5[O_2][Cl_2]$$

$$+ k_3 k_6[Cl_2][X] + k_4 k_6[O_2][X]\} = 2I k_2[H_2]$$

$$[H^\cdot] = \frac{2I k_2[H_2]}{k_3 k_6[Cl_2][X] + [O_2](k_2 k_4[H_2] + k_3 k_5[Cl_2] + k_4 k_6[X])}$$

$$[H^\cdot] = \frac{2I k_2[H_2]}{k_3 k_6[Cl_2][X] + [O_2](k_2 k_4[H_2] + k_3 k_5[Cl_2] + k_4 k_6[X])} \quad \text{---} \quad (B_1)$$

④ The rate of formation of HCl is

$$v_{HCl} = \frac{d[HCl]}{dt} = k_2[Cl^\cdot][H_2] + k_3[H^\cdot][Cl_2] \quad \text{—— E5}$$

from E2 we obtain

$$k_2[Cl^\cdot][H_2] = k_3[H^\cdot][Cl_2] + k_4[H^\cdot][O_2] \quad \text{—— E6}$$

Inserting E6 into E5, we get

$$v_{HCl} = \frac{d[HCl]}{dt} = k_3[H^\cdot][Cl_2] + k_4[H^\cdot][O_2] + k_3[H^\cdot][Cl_2]$$

$$= 2k_3[H^\cdot][Cl_2] + k_4[H^\cdot][O_2]$$

At low concentrations of oxygen the second term can be neglected.

$$2k_3[H^\cdot][Cl_2] \gg k_4[H^\cdot][O_2]$$

$$\approx 2k_3[H^\cdot][Cl_2]$$

Then $v_{HCl} = 2k_3[H^\cdot][Cl_2]$ —— E7

Introducing E4 into E7, we get

$$v_{HCl} = \frac{2k_2k_3[H_2][Cl_2]^{\frac{1}{2}}}{k_3k_6[Cl_2][X] + [O_2](k_2k_4[H_2] + k_3k_5[Cl_2] + k_4k_6[X])} \quad \text{—— E8}$$

(5) Division of numerator and denominator by $k_2 k_4$ yields

$$v_{HCl} = \frac{\frac{2k_2k_3}{k_2k_4}[H_2][Cl_2]I}{\frac{k_3k_6}{k_2k_4}[Cl_2][X] + [O_2]\left(\frac{k_2k_1}{k_2k_4}[H_2] + \frac{k_3k_5}{k_2k_4}[Cl_2] + \frac{k_4k_1}{k_2k_4}[X]\right)}$$

$$= \frac{2(k_3/k_4)I[H_2][Cl_2]}{\left(\frac{k_3k_6}{k_2k_4}\right)[Cl_2][X] + [O_2]\left\{[H_2] + \left(\frac{k_3k_5}{k_2k_4}\right)[Cl_2] + \frac{k_1}{k_2}[X]\right\}} \quad (E9)$$

This expression is of the form of the empirical equation given below

$$\frac{d[HCl]}{dt} = \frac{kI[H_2][Cl_2]}{m[Cl_2] + [O_2]([H_2] + n[Cl_2])}, \quad (E10)$$

the constants being related by

$$k = \frac{2k_3}{k_4}; \quad m = \frac{[X]k_3k_6}{k_2k_4}; \quad n = \frac{k_3k_5}{k_2k_4}$$

This scheme of reactions therefore gives a kinetic law (E9) that is essentially in agreement with the experimental rate equation (E10).