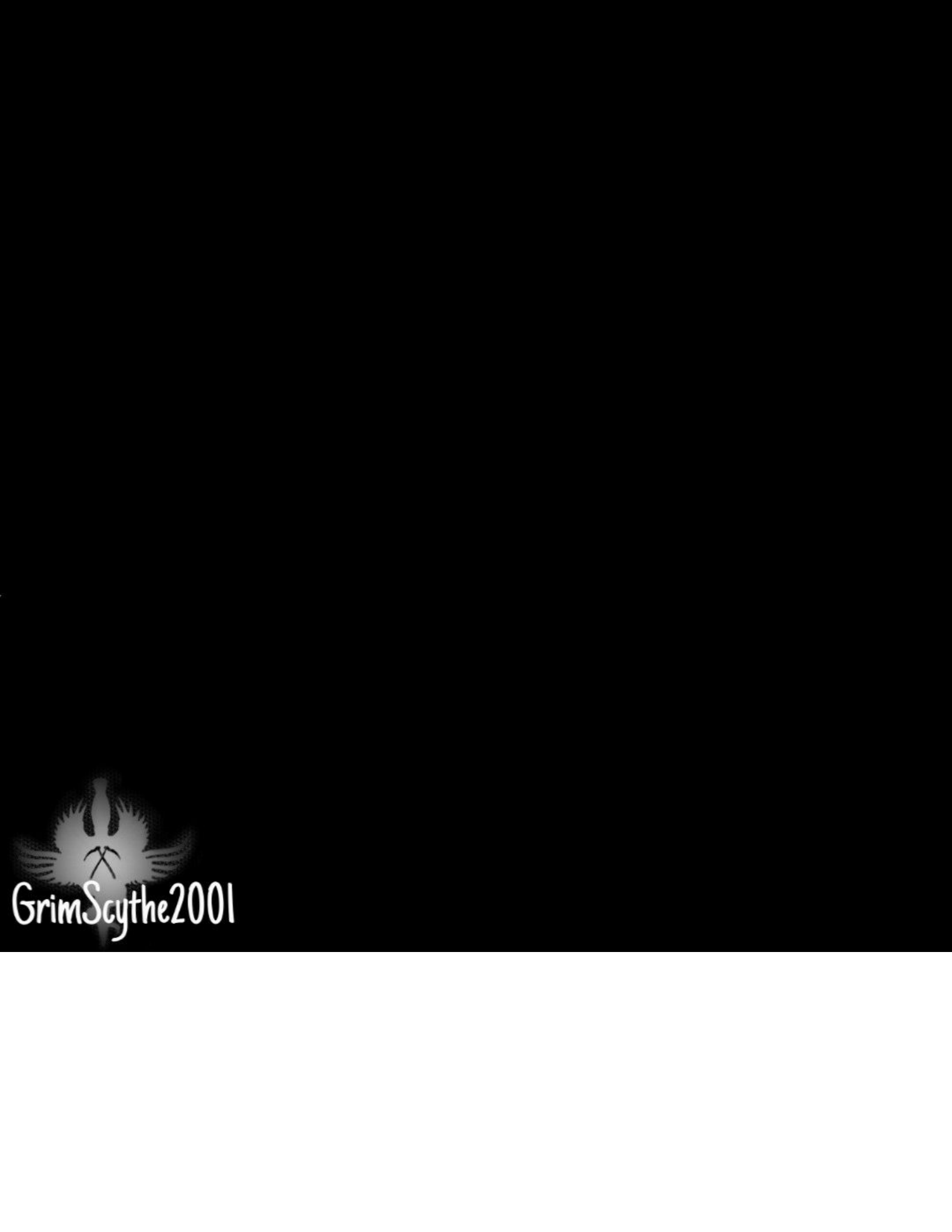
GrimScythe2001

Q.1. Derive the expression for overall rate of formation of NOCl.

→ $2NO + Cl_2 \longrightarrow 2NOCl$

i.e., $r = \frac{1}{2}\frac{d[NOCl]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[Cl_2]}{dt}$

Now,

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2$$

$$NOCl_2 + NO \xrightarrow{k_2} 2NOCl$$

So,

$$\frac{1}{2}\frac{d[NOCl]}{dt} = k_2[NOCl_2][NO] \quad -(i)$$

from steady state approximation

$$\frac{d[NOCl_2]}{dt} = 0$$

$$\text{i.e., } k_1[NO][Cl_2] - k_{-1}[NOCl_2] - k_2[NOCl_2][NO] = 0$$

$$\text{i.e., } [NOCl_2] = \frac{k_1[NO][Cl_2]}{k_{-1} + k_2[NO]} \quad -(ii)$$

Placing (ii) in (i),

$$\frac{1}{2}\frac{d[NOCl]}{dt} = k_2\left(\frac{k_1[NO][Cl_2]}{k_{-1} + k_2[NO]}\right)[NO]$$

$$\therefore \frac{d[NOCl]}{dt} = \frac{2k_1k_2[NO]^2[Cl_2]}{k_{-1} + k_2[NO]}$$

This is the required expression for rate of formation of NOCl.

Q. 2. Derive the expression for overall rate of formation of phorgene ($COCl_2$).

→

$$CO + Cl_2 \longrightarrow COCl_2$$

i.e., $$r = -\frac{d[CO]}{dt} = -\frac{d[Cl_2]}{dt} = \frac{d[COCl_2]}{dt}$$

Now,

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$$

$$CO + Cl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl \quad \text{(fast)}$$

$$COCl + Cl_2 \xrightarrow[\text{slow}]{k_3} COCl_2 + Cl$$

So,

$$\frac{d[COCl_2]}{dt} = k_3[COCl][Cl_2] \qquad -(i)$$

from steady state approximation,

$$\frac{d[COCl]}{dt} = 0$$

or, $$k_2[CO][Cl] - k_{-2}[COCl] - k_3[COCl][Cl_2] = 0 \qquad -(ii)$$

$$\therefore [COCl] = \frac{k_2[CO][Cl]}{k_{-2} + k_3[Cl_2]} \qquad -(iii)$$

Again, from steady state approximation,

$$\frac{d[Cl]}{dt} = 0$$

or, $$k_1[Cl_2] - k_{-1}[Cl]^2 - k_{-2}[CO][Cl] + k_{-2}[COCl] + k_3[COCl][Cl_2] = 0$$

Adding this equation to steady state equation of $[COCl]$ in (ii), we get,

$$k_1[Cl_2] - k_{-1}[Cl]^2 = 0$$

$$\therefore [Cl] = \left(\frac{k_1}{k_{-1}}[Cl_2]\right)^{1/2} \qquad -(iv)$$

Placing value of (iv) in (iii),

$$[COCl] = \frac{k_2[CO]}{k_{-2}+k_3[Cl_2]} \left(\frac{k_1}{k_{-1}}[Cl_2]\right)^{1/2} \quad \text{-(v)}$$

Placing this value (v) in rate expression (i), we get,

$$\frac{d[COCl_2]}{dt} = k_3 \left[\frac{k_2[CO]}{k_{-2}+k_3[Cl_2]} \left(\frac{k_1}{k_{-1}}[Cl_2]\right)^{1/2}\right][Cl_2]$$

Or, $$\frac{d[COCl_2]}{dt} = \frac{k_2 k_3 \left(\frac{k_1}{k_{-1}}\right)^{1/2}}{k_{-2}+k_3[Cl_2]} [CO][Cl_2]^{1/2}[Cl_2]$$

$$\therefore \frac{d[COCl_2]}{dt} = \frac{k_2 k_3 \left(\frac{k_1}{k_{-1}}\right)^{1/2}}{k_{-2}+k_3[Cl_2]} [CO][Cl_2]^{3/2}$$

$$\therefore r = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \frac{k_2 k_3 [CO][Cl_2]^{3/2}}{k_{-2}+k_3[Cl_2]}$$

This is the required expression for rate of formation of phorgene.