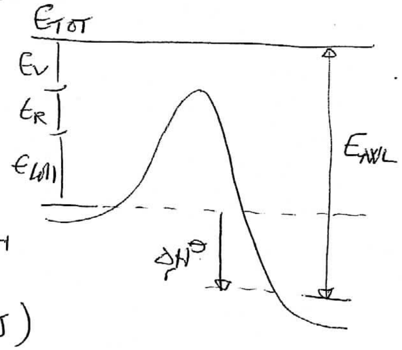
Molecular Reaction Dynamics

Crib

(1) (a) $E_{avl} = -\Delta_r H^{\ominus} + E_{coll} + E_v + E_R$



$\Delta_r H^{\ominus} = 149 - 319 = -170 \text{ kJ mol}^{-1}$ $(-2.82 \times 10^{-19} \text{ J})$

$E_{coll} = \frac{1}{2}\mu V_{rel}^2$

$\equiv 10.81 \text{ kJ mol}^{-1}$ $(1.79 \times 10^{-20} \text{ J})$

$V_{rel} = 800 \text{ ms}^{-1}$

$\mu = \frac{39 \cdot 254}{39 + 254} \text{ u}$

$= 5.61 \times 10^{-26} \text{ kg}$

$E_R = RT$ (assume equipartition of rot^n energy of I_2)

$= 2.49 \text{ kJ mol}^{-1}$ $(4.13 \times 10^{-21} \text{ J})$

$E_v \sim hc\omega_e \left(e^{\theta v/T} - 1\right)^{-1}$

$\equiv 1.425 \text{ kJ mol}^{-1}$ $(2.37 \times 10^{-21} \text{ J})$

$\theta v = \frac{hc\omega_e}{k_B} = 309 \text{ K}$

$\left(e^{\theta v/T} - 1\right)^{-1} = 0.555$

$E_{AVL} = 182 \text{ kJ mol}^{-1}$ $(3 \times 10^{-19} \text{ J})$

(b) $\sigma_R = \int_0^{b_{max}} P(b)\, 2\pi b\, db \simeq \pi b_{max}^2$ (assuming $P(b) = 1$ for $0 < b \leq b_{max}$)

$b_{max} = 7.4 \text{ Å}$

$|L|_{max} = \mu V_{rel} b_{max} = 5.61 \times 10^{-26} \times 800 \times 7.4 \times 10^{-10}$

$= 3.3 \times 10^{-32} = \hbar \sqrt{L(L+1)}_{(MAX)}$

$\simeq \hbar \left(L + \frac{1}{2}\right)_{MAX}$.

$L \simeq 312$

(c) $E_R' \simeq B_e' J'(J'+1)$ $\quad J' = L$ (assumed)

$= 5957 \text{ cm}^{-1}$

$\equiv 71.2 \text{ kJ mol}^{-1}$ $(1.2 \times 10^{-19} \text{ J})$

(Nb., $J' = 312$ is energetically accessible.)

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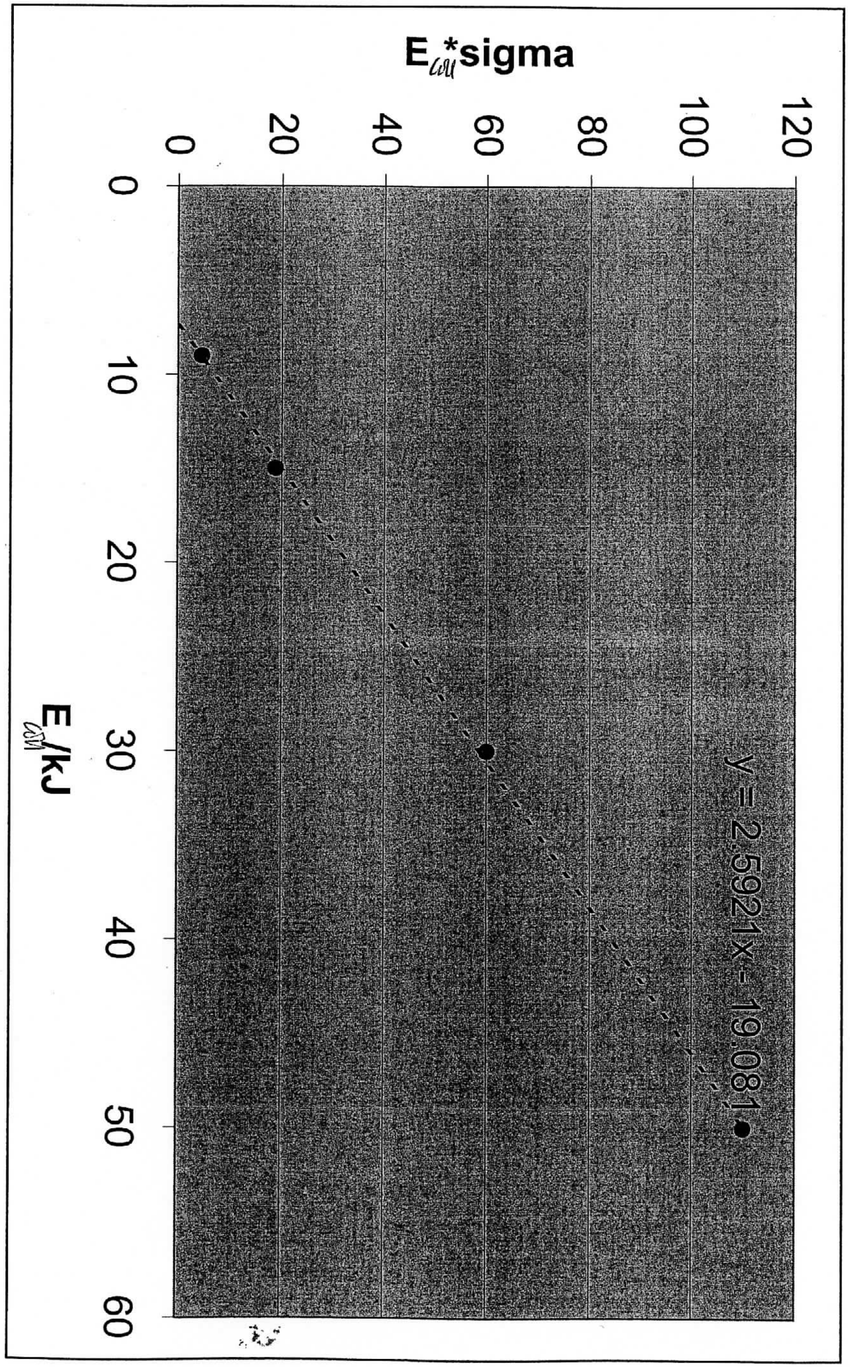
(2) $\sigma_R(E_{coll}) = \pi d^2 \left(1 - \frac{E_0}{E_{coll}}\right)$

$E \times \sigma_R(E_{coll}) = \pi d^2 \left(E_{coll} - E_0\right)$

Plot $E_t\, \sigma_R(E_{coll})$ vs E_{coll} (see attached)

$\pi d^2 = 2.6 \text{ Å}^2$

$E_0 = 7.4 \text{ kJ mol}^{-1}$



Question 2

2(b) $$k(T) = \langle V_{rel} \rangle \int_{E_0}^{\infty} \frac{E_{coll}}{kT} \pi d^2 \left(1 - \frac{E_0}{E_{coll}}\right) e^{-E_{coll}/kT} \frac{dE_{coll}}{kT}$$

$x = \varepsilon / kT \qquad a = E_0 / kT$

$dx = \frac{1}{kT} d\varepsilon$

$$k(T) = \langle V_{rel} \rangle \int_a^{\infty} \pi d^2 (x - a) e^{-x} \, dx$$

$$= \langle V_{rel} \rangle \pi d^2 e^{-a}$$

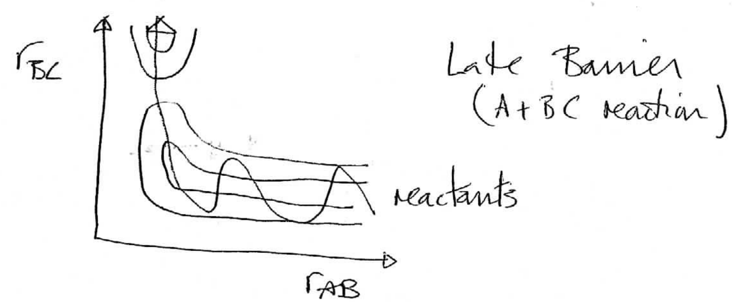
$$\boxed{k(T) = \langle V_{rel} \rangle \pi d^2 e^{-E_0/kT}}$$

Simple collision Theory!

(c) Factors

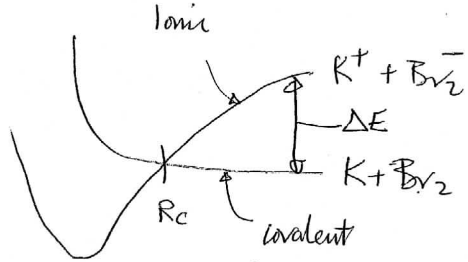
① More energy in HCl (v=1) than v=0.

② Shape of the PES. To favour enhancement of cross-section by vibration, would a Late barrier!



(3) Harpoon rxn

(a)



$V_{covalent} \sim 0$ (van der Waals at long range)

$$V_{ionic} = \Delta E - \frac{e^2}{4\pi\varepsilon_0 R}$$

Curve crossing occurs ~~at~~ when $V_{covalent} = V_{ionic}$!

$$\Delta E = e^2 / 4\pi\varepsilon_0 R_c$$

$$R_c = \frac{e^2}{4\pi\varepsilon_0 \Delta E} \quad (1.6 \times 10^{-19})$$

$$\underline{R_c = 8.0\ \text{Å}}$$

$$\Delta E = IP - EA$$
$$= 418.8 - 245$$
$$= 173.8\ \text{kJ mol}^{-1}$$
$$\equiv 2.886 \times 10^{-19}\ \text{J}$$

$\sigma_R \simeq \pi R_c^2$ (Assuming $P(b) = 1$ again)

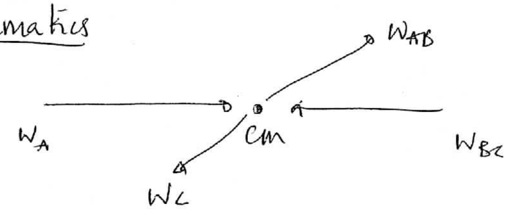
$\simeq 200\ \text{Å}^2$ (Huge).

(b) I.P.'s decrease from Na to Cs

∴ σ_R increases (because $\Delta E \downarrow$)

(c) Some details of crossed molecular beam experiments described in Lectures (and recommended texts).

(4) Kinematics



Momentum Conservation

$$m_A \underline{w_A} = -m_{BC} \underline{w_{BC}} \quad (1)$$
$$m_C \underline{w_C'} = -m_{AB} \underline{w_{AB}'} \quad (2)$$

$$E_{cm} = \tfrac{1}{2} m_A w_A^2 + \tfrac{1}{2} m_{BC} w_{BC}^2$$

Substitute for w_A using (1) ($M = m_A + m_{BC}$)

$$\boxed{E_{cm} = \tfrac{1}{2} m_{BC} \frac{M}{m_A} w_{BC}^2}$$

Similarly for E'

$$E_{cm}' = \tfrac{1}{2} m_C w_C'^2 + \tfrac{1}{2} m_{AB} w_{AB}'^2$$

$$\boxed{E_{cm}' = \tfrac{1}{2} m_C \frac{M}{m_{AB}} w_C'^2}$$

$$\therefore \boxed{\frac{E_{cm}'}{E_{cm}} = \cos^2\beta \left(\frac{w_C'}{w_{BC}}\right)^2}$$

with $\cos^2\beta = \dfrac{m_A m_C}{m_{AB} m_{BC}}$

skew angle

In Spectator limit when $W_C' = W_{BC}$

$$E_{coll}' = \cos^2\beta \, E_{coll}$$

So (i) $E_{coll}' = E_{coll}$ when $\cos^2\beta = 1$

Occurs when $\beta \sim 0°$. ie, for a light atom transfer rxn. eg $Cl + HI$ Q5 exothermicity must be released into internal modes

(ii) $E_{coll}' \sim 0$ when $\cos^2\beta = 0$

(light attacking/departing atom)

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(5) (a) Principally laser pump-probe methods (see lecture notes)

(b) Points about specific reactions!

(i) Kinematics! skew angle for $H + Cl_2 \sim 90°$, while for $Cl + HI$ is $\sim 10°$

(ii) Polanyi's rules really only work for $\beta \sim 90°$, ie for $H + Cl_2$. Late barrier in this case

(iii) For $Cl + HI$, small skew angle is responsible for high vibrational excitation, in spite of latish barrier (related to Q4 above)

(iv) $H + Cl_2 \rightarrow$ rebound dynamics (small σ + b's)
$Cl + HCl \rightarrow$ stripping dynamics (large σ + b's)

5(c) $Ba + HI \longrightarrow BaI(v', j') + H$

Ang. Mom conservation in this case $\underline{L} \longrightarrow \underline{j}'_{BaI}$

$P(L) \simeq P(J') \leftarrow$ measure using LIF

$\equiv P(b)$

(L: orbital ang mom quantum number)

$|\underline{L}| = \mu v_{rel} b = \hbar\sqrt{L(L+1)} \sim \hbar(L + \tfrac{1}{2})$

$L \sim \dfrac{\mu v_{rel} b}{\hbar} = 420$ (most probable 'b')

$\mu = \dfrac{137.3 \cdot 127.9}{265.2}$ u $= 1.1 \times 10^{-25}$ Kg

$b \sim \dfrac{\hbar\, 420}{\mu v_{rel}} = 4.1 \times 10^{-10}$ M

$\sigma_R \simeq \pi b^2 = 53$ Å^2

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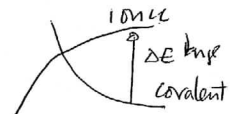
(6) Things to consider

$K + I_2$ – Forward scattering (Harpoon rxn with large cross-section → rxn at large b)

– KI is born internally excited. Energy released early along rxn coordinate.

<u>K + CH_3I</u> — Backward Scattering (rebound dynamics) small cross-section + rxn at low b's.

— Harpoon rxn but EA of CH_3I is negative. <u>Barrier to reach r_c</u> !



— KI born <u>translationally</u> excited. Late release of exothermicity (late barrier)

<u>$S(^1D) + H_2$</u> — Forms a rotating collision complex ($H_2S^{\oplus}$)

— Leads to Forward-backward symmetry in the DCS.

— [Relative height of DCS at 0°, 180° versus 90° depends on angular momentum conservation L → j' or L'.]

7 (a) — OH + D_2 → HOD + D is isoelectronic with F + H_2 and dynamics are similar.

— Rebound reaction — early barrier — population inversion in HOD(v).

— <u>Extra feature</u> is that none of the energy is released into <u>OH</u> vibration. The OH bond acts as a '<u>Spectator</u>'. Example of <u>Selective</u> disposal of energy in newly formed bond.

— [Reverse reaction H + HOD also discussed in lectures — provides example of <u>mode selective</u> chemistry. Role / lack of role of IVR also discussed briefly.]

(b) — Cf F – pH_2^- again. Photoselection spectroscopy of the anion suggests $F–H_2^{\ddagger}$ T.S. is bent (linear – bent transition)

$OH \cdots H_2^-$ (H_3O^-) has also been studied.

— Need anion geometry to be similar to neutral T.S. geometry if you want to probe T.S. structure. So the method is not entirely general.