Hot-Atom Chemistry

In (n, γ) type nuclear rx^n's, the nucleus of the target atom captures a thermal neutron & forms a compound nucleus of high excitation energy. The compound nucleus returns to the G.S. with the emission of one or more γ-photons, and the residual nucleus undergoes "Compton recoil" & is therefore projected with a certain amount of energy, called "RECOIL ENERGY". E_R

The value of E_R can be calculated by the conservation of momentum

$$p = P$$

p → momentum of the emitted particle or photon
P → " " " recoil nucleus/atom

The momentum of a recoil atom is

$$P = MV$$

where M is the mass of the recoil atom, & V is its velocity.

The K.E. of the recoil ~~energy~~ atom, E, is

$$E = \frac{1}{2} MV^2$$

$$\text{or} = \frac{M^2 V^2}{2M} \quad \text{after multiplying with } M$$

but we know that $MV = P$

so, $$\boxed{E = \frac{P^2}{2M}}$$ but $P = p$

so, $$\boxed{E = \frac{p^2}{2M}}$$ Recoil Energy

but $p_\gamma = E_\gamma / c$

E_γ = Energy of γ-ray
c = velocity of light

$$E_R = \frac{p^2}{2M}$$

$$E_R = \frac{E_\gamma^2}{2MC^2}$$

$$= \frac{536 \times 10^{-6} E_\gamma^2}{M} \text{ MeV}$$

Following possibilities of emission exists:
(i) emission of heavy particles (α, p, n, ...)
(ii) γ - rays
(iii) electrons
(iv) β - decay processes

Emission of α - particle:

$$P_\alpha = m_\alpha v_\alpha$$

where m = mass & v = velocity of α - particle.

R.E. of the recoil atom
(Recoil Energy)

$$E_R = \frac{m_\alpha^2 v_\alpha^2}{2M}$$

since the K.E. of the α particle, E_α is equal to

$$E_\alpha = \frac{1}{2} m_\alpha v_\alpha^2$$

$$\boxed{E_R = \frac{m_\alpha}{M} E_\alpha}$$ in MeV

Emission of γ - rays: The momentum of a photon can be given by

$$p_\gamma = \frac{E_\gamma}{c}$$

where E_γ = energy of γ - ray
c = velocity of light

Recoil Energy $$\boxed{E_R = \frac{E_\gamma^2}{2Mc^2}}$$

if E_γ is in MeV, c is in cm/sec, mass of recoil atom in AMU are substituted

$$\boxed{E_R = \frac{536 \times 10^{-6} E_\gamma^2}{M}}$$ in MeV

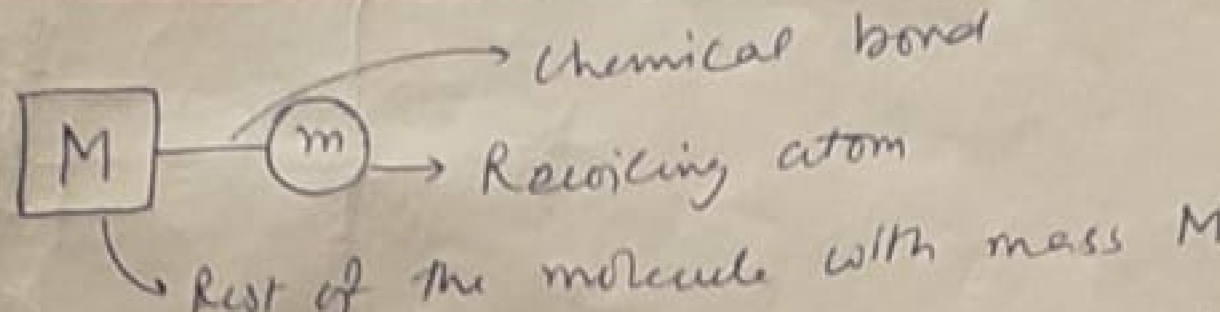
Ex. When ^{127}I is irradiated with neutrons in a $^{127}I(n, \gamma)^{128}I$ rx^n. γ-ray of 7 MeV are emitted. The recoil energy of ^{128}I nucleus will be

$$E_R = \frac{536 \times 10^{-6} E_\gamma^2}{M}$$

$$= \frac{536 \times 10^{-6} \times (7)^2}{128} = 205 \times 10^{-6} \text{ MeV}$$

or 205 eV

Recoil of an Atom in a molecule:



The recoiling energy of the atom 'm' is transmitted to the whole atom since it is attached to M by a chemical bond. This energy can affect the whole molecule by producing a translational energy and also excitation mainly in the form of vibrations. Thus,

$$E_{Recoil} = E_{excitation} + \underbrace{\tfrac{1}{2}(m+M)V^2}_{\text{translational energy}}$$

where V is the velocity of translation of the molecule

Now, conservation of momentum demands that

$$mv = (m+M)V$$

$$\therefore V = \frac{mv}{m+M}$$

$$E_{Recoil} = E_{excitation} + \frac{1}{2}(m+M) \cdot \frac{m^2 v^2}{(m+M)^2}$$

$$= E_{ex.} + \frac{1}{2} m v^2 \frac{m}{(m+M)}$$

$$E_{Recoil} = E_{excitation} + E_{Recoil} \cdot \frac{m}{m+M}$$

or $$E_{excitation} = E_{Recoil}\left[1 - \frac{m}{m+M}\right]$$

$$\boxed{E_{excitation} = E_{Recoil}\,\frac{M}{m+M}}$$

Three situations exist:

(1) Thus when $M >> m$ then

$$E_{excitation} = E_{Recoil}$$

and all of the recoil energy can be used for rupturing a chemical bond

(2) On the contrary if $m >> M$

then $$\frac{M}{m+M} \approx 0$$

$\therefore$ $E_{excitation} \sim 0$ (close to zero)

& the entire recoil energy is converted into the energy of the translational motion of the entire molecule, & the chemical bond remains INTACT.

(3) & if $m = M$ then

$$E_{excitation} = \frac{1}{2} E_{Recoil}$$

only half of the recoil energy can be spent to break a chemical bond.

Ex. Calculate the excitation energy of HCl molecule when a ^{35}Cl gives a (n,γ) rxn with 6.2 MeV γ-ray emission. Find out if H–Cl bond (strength = 4.4 eV) would break during the rxn.

$$E_{Recoil} = \frac{E_\gamma^2 \times 536 \times 10^{-6}}{M}$$

$$E_{Recoil} = \frac{(6.2)^2 \times 536 \times 10^{-6}}{36} = 572 \times 10^{-6}\ \text{MeV}$$

or 572 eV

Now $E_{ex} = E_R \frac{M}{m+M}$

$E_{ex} = 572 \frac{1}{1+36}$

$= 15.5\ eV$

As H–Cl energy is only 4.4 eV it will break

Data for some Molecules ⇒ (n, γ) type Rx^ns.

X Halogen	E_γ (MeV)	H—X (eV)		C_2H_5—X (eV)	
		BDE	Excit.	B.D.E.	Excitation
Cl	6.2	4.4	15.5	3.1	235
Br	5.1	3.7	2.2	2.6	45
I	4.8	3.0	0.8	2.0	18

Thus for H—X molecule, the bond will break for H—Cl but not for H—Br or H—I because $m >> M$.

In C_2H_5—X the bond will break in all cases since $m \sim M$ comparable and substantial amount of recoil energy is spent in bond breaking.

Historically, Szilard & Chalmers (1934) showed that after irradiation with neutrons, the C_2H_5-I bond is broken & the ^{128}I could be separated from ^{127}I chemically to affect an isotope separation as follows:

$$C_2H_5-{}^{127}I \xrightarrow{n,\gamma} C_2H_5{}^{128}I^{*}$$

$$\downarrow$$

$$Ag^{128}I^{*} \xleftarrow{Ag^+} {}^{128}I^{*\ominus} \xleftarrow{\text{Reduction}} C_2H_5^{\cdot} + {}^{128}I^{*}_{\odot}$$

The conditions to be fullfilled are:

(i) The E_{Recoil} & Excit. must be high enough to break the bond

(ii) the broken atom must exist independently for a while & should not re-combine with the original molecule immediately

(iii) should not exchange isotopically with non-radioactive starting reagents

(iv) A quick method of separation should be available.