*Supplement #5:Free Radical Substitution of Halogens on Methane*

*Chemistry 3514 Organic Chemistry I*

**5.1 THE FACTS: *What the Experimentalists Tell Us* (not in text)**

**Overall Reaction:** (note: Δ or hν => heat or light; X2 =F2, Cl2, Br2 or I2, *xs*= excess)

hυ

*xs*  X2 + CH4 CH4-mX + m HX, m =1,2,3,4

**Observed Behavior Patterns Summarized:**

1) reaction will only go at >250oC in dark or with input of ultraviolet (uv) light.

2) uv wavelength required is near that for dissociation wavelength for X2 .

3) in excess X2 , a single photon (hν) event causes thousands of halogenations.

(=> photo yield >>>>1, e.g 1000-5000 halogenated methane molecules/1 photon of hν.

4) O2 causes halogenation reaction to slow or stop.

5) reactivity rate follows the trend : F2 > Cl2 > Br2 > I2 .

**5.2 EXPLAINING THE FACTS: *Mechanism Of Halogenation Of Methane (see also: pp.151-152)***

**Currently Accepted Mechanistic steps: a Free Radical Reaction**

(**X\*, CH3\*** etc => free radicals of **X**, **CH3** etc. )

***step # elementary reaction commentary***

***hv***

1  **X2 ------> 2X\*** chain-initiation (rather like making a cancer cell)

2 **X\* + CH4 -------> HCl + CH3\*** chain propagation....

3 **X2 + CH3\* -------> CH3X + X\*** (one begets another... ! Note that radicals

**...... etc. etc.** are implicated in aging and cancer)

Multiple substitutions of X can occur on originally generated CH3X by same mechanism, e.g.:

2’ **X\* +CH3X -------> CH2X\* + HX**

3’ **CH2X\* + X2 -------> CH2X2 + X\***

Then:

2” **X\* +CH2X2 -------> CHX2\* + HX**

3” **CHX2\* + X2 -------> CHX3 + X\* etc**

The process is terminated by radical-radical recombination or quenching by O2.

4a **X\* + X\*---> X2**

4b**CH3\* + CH3\* --->CH3CH3**chain termination

4c **CH3\* + Cl\*---> CH3Cl**

4d **CH3**\* **+ O2-----> CH3OO\*** (final `peroxyl’ radical is rather stable => it sucks

peroxyl radical energy from CH3\* and takes it `off the board’ similar to a radical-radical termination)

**5.3 *Mechanism Seen Through* the *`Activated Complex’ or Energy Diagram Picture1***

***(text discusses this generally on pp. 169-174)***

**activated, 5-coordinate X-->CH3----H complex**

**at top of first hill**

**M**= metastable state

**P** = product state

**Potential**

**Energy** **M**

*activation*

**CH3\* +HX**

*barrier*

*Heat (Enthalpy) of Reaction*

**P**

**CH3X + X\***

Up the big hill and down to M Up the little hill and down to P

**CH4  + X\*🡪**

**X2 + CH3\*🡪**

**step 2 step 3** .....etc

**Progress of Reaction**

(aka Reaction Coordinate)

1 also called the Eyring-Polanyi model 2 internal methyl group is in `sp2’ excited hybrid state

**5.4 SPIN OFF OF THE MODEL: What the Activated Complex looks like (see text pp 204-206)**

Hammond Postulate



**CASE**

**Reactant-like barrier low easy to convert**

**“***exergenic’*



**Product-like barrier high reluctant to `release**

**‘***endergonic’*