HOMEWORK ASSIGNMENT #5 ORGANIC CHEMISTRY I (20 pts)

**free radical reactions of ozone & higher alkanes**

**(due Monday 10 October)**

**Your name:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (1 pt)**

**5.1a.** In early experiments in the l920s, Fritz Paneth and co-workers at the University of Berlin passed

tetramethyl lead, (CH3)4Pb, down an evacuated glass tube. They heated the tube with a coil of hot wire wrapped around the outside of the glass. Where ever the coil was wrapped, a shiny deposit of pure Pb metal appeared nearby and a stream of ethane (CH3-CH3) was detected at the exit end of the tube as sketched below. (3 pts)

Pb **Hot wire**

**Pb(CH3)4 in** **CH3-CH3 out**

**Pb metal deposit forms**

Suggest a mechanism for this set of observations.

Formation of Pb requires decomposition of tetramethyl lead: 1) Pb(CH3)4🡪 Pbo +4CH3\*

Observation of CH3-CH3 requires combination of CH3\* 2) 2CH3\* 🡪 2CH3-CH3

5**.1b.** If the hot wire is moved up stream closer to the original source of the Pb(CH3)4, and more Pb(CH3)4 is flowed

into the tube the original Pb metal deposit disappears, a new one forms were the wire is placed, and, mostly

just Pb(CH3)4 exits the tube.

**New Pb deposit forms old Pb deposit slowly disappears**

**Pb(CH3)4 in**

**Pb(CH3)4 out Hot wire**

**moved upstream**

**Explain these results in terms of the mechanism in 5.1a you propose. (3 pts)**

**Hot wire’s movement upstream creates same mechanism proposed in 5.1a.**

**However, the CH3\* radicals encounter Pb down stream and carry out the reaction:**

1. **Pb + 4CH3\* 🡪 Pb(CH3)4 (g) explaining which old Pb disappears and Pb(CH3)4 only exits**

**5.2 Drawn and quartered… 3 pts**

Sketch on the same plot below the reaction coordinate diagrams of Br and Cl with CH4 , making sure to emphasize where they differ.

Energy

Metastable state

Br

Cl

Chlorine reaches activated complex sooner and with less activation energy than Bromine. It also reaches the end of step 3 at a lower potential (more stable). Exaggerate the differences for clarity in any sketch .

**CH4 + Br or Cl**

**reaction progress**

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**5.3. Circle the carbon at which the most rapid chlorination is expected**

**in each of the two structures below ( 2 pts)**



**5.4) Productive thinking (4 pts)**

Photochemical bromination of 2,2,4-trimethylpentane yields 4 different monobromides. Draw them below

A (1o) B (1o)





C(2o) D (3o)





**5.5**) Compute the expected % yields of A-D you’ve drawn above given the following relative yield (R) data below: (see also- exercise 7 and supplement 7). 5 pts

**Site degree** **Relative yield/H for radical Bromination**

1o  1

20` 50

30 750

raw, unscaled yield % yield

**Compound expected % yield =y=# H \* R 100\* y/sum**

A \_\_\_\_\_1.04\_\_\_\_\_\_\_\_\_ 9\*1 =9 1.04

B \_\_\_\_\_\_0.7\_\_\_\_\_\_\_\_\_\_ 6\*1=6 0.7

C \_\_\_\_\_11.6\_\_\_\_\_\_\_\_\_\_ 2\*50=100 11.6

D \_\_\_\_\_86.7\_\_\_\_\_\_\_\_\_ 1\*750=750 86.7

sum= 865

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