# Chemistry 125   Fifth Examination       Name _____
## February 2, 2006

**1.** (2 min)   Draw the mechanism for the **propagation** steps in the free-radical chain "machine" for halogenation of the alkane R-H by the halogen molecule X-X.

**2.** (2 min) In discussing the selectivity of free-radical halogenation of n-butane, the text presents data both for **chlorination in the vicinity of room temperature** and for **bromination at about 1.5 times room temperature**.
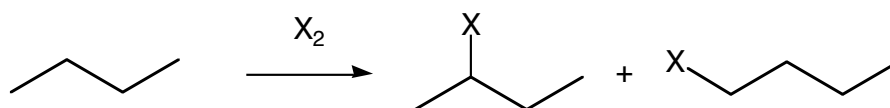


In one case the ratio of the two products is $72/28 = $ **2.6** ; in the other case their ratio is $98/1.8 = $ **54**.

**CIRCLE** the ratio that is for **CHLORINATION** (no explanation necessary).

**Also draw a double arrow ($\Downarrow$)** in your scheme for Question 1
**to indicate which step** determines the ratio of primary to secondary product.

**3.** (9 min) Use the data Question 2 to estimate values for the ***difference*** **in energy of activation ($\Delta\Delta H^{\ddagger}$)** for abstraction of **primary and secondary H by Cl•** . [Feel free to make reasonable numerical approximations, but explain what you are doing. The log table at the right is plenty precise.]       **Repeat** for abstraction by Br•.

| n | log(n) |
|---|--------|
| 1 | 0.00 |
| 2 | 0.30 |
| 3 | 0.48 |
| 4 | 0.60 |
| 5 | 0.70 |
| 6 | 0.78 |
| 7 | 0.85 |
| 8 | 0.90 |
| 9 | 0.95 |
| 10 | 1.00 |

**4.**   (7 min) Explain how your answer to Question 3 illustrates the Hammond Postulate.  You may want to use data from
the tables on the last two pages of this exam to refresh your memory about bond dissociation energies.

**5.**   (6 min) Why would one expect to obtain different isomers of butyne after equilibrating with an amide base (like
KNHCH$_3$) than after equilibrating with an alkoxide base (like KOCH$_3$)?

**6.**   (3 min) What reaction did Moses Gomberg use to prepare tetraphenylmethane?

**7.**   (6 min)  The terms "Markovnikov" and "anti-Markovnikov" can be applied to regiochemical selectivity in the ionic and free-radical addition of HBr to 1-propene.  Although elementary textbooks suggest that the bias is 100% (all one product), there must be some of minor product present in each case.   **Explain in terms of orbital mixing** which mechanism (ionic or free-radical) should give a stronger bias in favor of its preferred product?

**8.**   (3 min)  What is remarkable about the R-R' bond dissociation energies in the ten hydrocarbons [boxed on p. 6]  that cleave to form any combination of the methyl, ethyl, iso-propyl and t-butyl radicals (after correcting for strain energy of the starting material using molecular mechanics)?  Mention also the trend in R-H and R-OH BDE values.

**9.**  (6 min)  Explain how the "photoelectron spectrum" of the $CH_3O^-$ anion allowed accurate determination
of the bond dissociation energy of $CH_3O$-H.   It would help to draw an energy diagram.



CH₃O⁻
FROM CH₃OD
488 nm (2.540 eV)
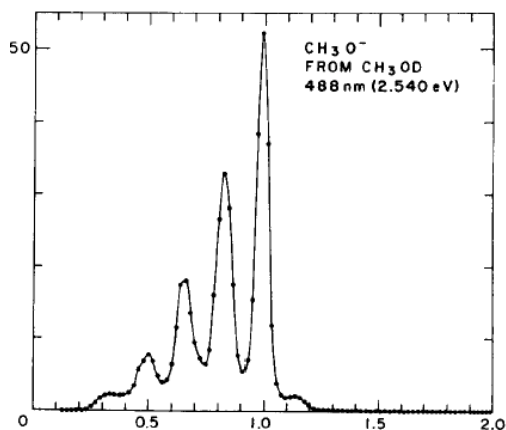
**10.**  (6 min)  Assign numbers 1-4 to indicate the relative reactivity of the following alkenes in addition of HCl.
Use **1** for the **most** reactive.  Use this ranking to **describe three different influences** on reactivity.

$CH_2\!\!=\!\!CH$
$OCH_3$

$CH_2\!\!=\!\!CH$
$CH_3$

$CH_2\!\!=\!\!CH_2$

$CH_2\!\!=\!\!CH$
$CH_2Br$
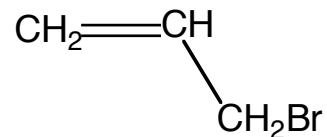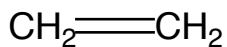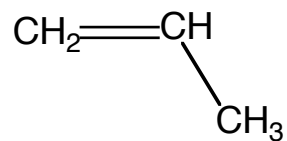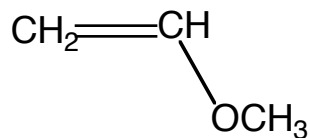
Bond Dissociation Energies of Organic Molecules   *Blanksby and Ellison*

## Table 1. Molecular Bond Dissociation Energies for RH → R + H: Experimental Bond Enthalpies and Radical Heats of Formation at 298 K

| RH | $DH_{298}$ (kcal mol⁻¹) | $\Delta_f H_{298}(R)$ (kcal mol⁻¹) | ref | RH | $DH_{298}$ (kcal mol⁻¹) | $\Delta_f H_{298}(R)$ (kcal mol⁻¹) | ref |
|---|---|---|---|---|---|---|---|
| **Inorganics** | | | | | | | |
| $H_2$ | 104.206 ± 0.003 | 52.103 ± 0.003 | 4 | OH⁻ → O⁻ + H | 110.21 ± 0.07 | −33.23 ± 0.07 | 34 |
| HF | 136.25 ± 0.01 | 18.83 ± 0.17 | 6 | OH⁺ → O + H⁺ | 115.2 ± 0.1 | 59.55 ± 0.02 | 34 |
| HCl | 103.15 ± 0.03 | 29.03 ± 0.04 | 9 | $H_2S$ | 91.2 ± 0.1 | 34.2 ± 0.2 | 6 |
| HBr | 87.54 ± 0.05 | 28.62 ± 0.06 | 9 | SH | 84.1 ± 0.2 | 66.2 ± 0.3 | 6 |
| HI | 71.32 ± 0.06 | 26.04 ± 0.08 | 9 | H−NO | 49.5 ± 0.7 | 21.8 ± 0.1 | 4 |
| H−CN | 126.3 ± 0.2 | 105.0 ± 0.7 | 6 | H−ONO (trans) | 79.1 ± 0.2 | 8.2 ± 0.1 | 4 |
| $NH_3$ | 107.6 ± 0.1 | 44.5 ± 0.1 | 6 | H−ONO₂ | 101.7 ± 0.4 | 17.6 ± 0.3 | 35 |
| $H_2O$ | 118.82 ± 0.07 | 8.86 ± 0.07 | 34 | $SiH_4$ | 91.7 ± 0.5 | 47.9 ± 0.6 | 9 |
| OH | 101.76 ± 0.07 | 59.55 ± 0.02 | 34 | $GeH_4$ | 83 ± 2 | 53 ± 2 | 9 |
| **Hydrocarbons** | | | | | | | |
| $CH_4$ | 104.99 ± 0.03 | 35.05 ± 0.07 | 31 | $CH_2CH$−H | 110.7 ± 0.6 | 71.1 ± 0.7 | 6 |
| $CH_3$ | 110.4 ± 0.2 | 93.3 ± 0.2 | 31 | HCC−H | 133.32 ± 0.07 | 135.6 ± 0.2 | 36 |
| $CH_2$ | 101.3 ± 0.3 | 142.5 ± 0.2 | 9 | $C_6H_5$−H | 112.9 ± 0.5 | 80.5 ± 0.5 | 6 |
| CH | 80.9 ± 0.2 | 171.3 ± 0.1 | 9 | $C_6H_5 \rightarrow o\text{-}C_6H_4 + H$ | 78 ± 3 | 106 ± 3 | 37 |
| $CH_3CH_2$−H | 101.1 ± 0.4 | 29.0 ± 0.4 | 10 | $C_6H_5 \rightarrow m\text{-}C_6H_4 + H$ | 94 ± 3 | 122 ± 3 | 37 |
| $(CH_3)_2CH$−H | 98.6 ± 0.4 | 21.5 ± 0.4 | 10 | $C_6H_5 \rightarrow p\text{-}C_6H_4 + H$ | 109 ± 3 | 138 ± 3 | 37 |
| $CH_3CH_2(CH_3)CH$−H | 98.2 ± 0.5 | 16.1 ± 0.5 | 10 | $CH_2CHCH_2$−H | 88.8 ± 0.4 | 41.4 ± 0.4 | 38 |
| $(CH_3)_3C$−H | 96.5 ± 0.4 | 12.3 ± 0.4 | 10 | $C_6H_5CH_2$−H | 89.8 ± 0.6 | 49.7 ± 0.6 | 38 |
| **Alcohols** | | | | | | | |
| H−$CH_2OH$ | 96.1 ± 0.2 | −4.08 ± 0.2 | 16 | $CH_3CH_2O$−H | 104.7 ± 0.8 | −3.6 ± 0.8 | 6 |
| $CH_3O$−H | 104.6 ± 0.7 | 4.3 ± 0.7 | 6 | $(CH_3)_2CHO$−H | 105.7 ± 0.7 | −11.5 ± 0.7 | 6 |
| $CH_3S$−H | 87.4 ± 0.5 | 29.8 ± 0.4 | 39,40 | $(CH_3)_3CO$−H | 106.3 ± 0.7 | −20.5 ± 0.7 | 6 |
| H−$CH_2SH$ | 94 ± 2 | 36 ± 2 | 39,40 | $C_6H_5O$−H | 90 ± 3 | −58 ± 3 | 41 |
| **Peroxides** | | | | | | | |
| HOO−H | 87.8 ± 0.5 | 3.2 ± 0.5 | 14 | $CH_3CH_2OO$−H | 85 ± 2 | −6.8 ± 2.3 | 42 |
| $CH_3OO$−H | 88 ± 1 | 4.8 ± 1.2 | 42 | $(CH_3)_3COO$−H | 84 ± 2 | −25.2 ± 2.3 | 42 |
| **Carbonyls** | | | | | | | |
| H−CHO | 88.144 ± 0.008 | 10.1 ± 0.1 | 6 | H−COOH is ≥ | 96 ± 1 | −46.5 ± 0.7 | 45 |
| $CH_3C(O)$−H | 89.4 ± 0.3 | −2.4 ± 0.3 | 43 | $CH_3COO$−H | 112 ± 3 | −43 ± 3 | 44 |
| H−$CH_2CHO$ | 94 ± 2 | 2.5 ± 2.2 | 9 | $C_6H_5COO$−H | 111 ± 4 | −12 ± 4 | 44 |
| HCOO−H | 112 ± 3 | −30 ± 3 | 44 | | | | |

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## Table 2. Experimental Bond Dissociation Enthalpies, $DH_{298}$ (kcal mol$^{-1}$)$^a$

| | methyl CH$_3$ | ethyl CH$_2$CH$_3$ | isopropyl CH(CH$_3$)$_2$ | tert-butyl C(CH$_3$)$_3$ | vinyl CHCH$_2$ | allyl CH$_2$CHCH$_2$ | phenyl C$_6$H$_5$ | benzyl CH$_2$C$_6$H$_5$ | methoxy CH$_3$O | formyl HC(O) | acetyl CH$_3$C(O) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 104.9(0.1) | 101.1(0.4) | 98.6(0.4) | 96.5(0.4) | 110.7(0.7) | 88.8(0.4) | 112.9(0.6) | 89.7(0.6) | 104.6(0.7) | 88.1(0.2) | 89.4(0.3) |
| F | 115(4)$^a$ | — | 110.6(0.5) | — | 123.3(0.8) | — | 127.2(0.7) | 98.7(0.7)$^a$ | — | — | 122.2(0.9) |
| Cl | 83.7(0.1) | 84.8(0.5) | 85.2(0.5) | 84.9(0.7) | 91.2(0.7) | — | 97.1(0.6) | 74(1) | — | — | 84.7(0.4) |
| Br | 72.1(0.3) | 72.4(0.6) | 73.9(0.7) | 72.6(0.6) | 80.8(0.8) | 59(1) | 84(1) | 63(1) | — | — | 71.7(0.3) |
| I | 57.6(0.4) | 56.9(0.7) | 57(1) | 55.6(0.9) | — | 45.6(0.9) | 67(2) | 51(2) | — | — | 53.8(0.7) |
| HO | 92.1(0.1) | 94.0(0.4) | 95.5(0.4) | 95.8(0.4) | — | 80.1(0.6) | 112.4(0.6) | 82.6(0.7) | — | 109.5(0.2) | 109.9(0.7) |
| CH$_3$O | 83.2(0.9) | 85(1) | 85.8(0.5) | 84(1) | — | — | 101(1) | — | 38(1) | 99.6(0.9) | 100(1) |
| NH$_2$ | 85.2(0.3) | 84.8(0.4) | 86.0(0.4) | 85.7(0.5) | — | — | 104.2(0.6) | 71.7(0.7) | — | — | 99.1(0.4) |
| CN | 122.4(0.7) | 121.6(0.8) | 120.9(0.5) | 117.8(0.8) | 133(1) | 108.7(0.9) | 134(1) | — | 42(1) | — | — |
| NO$_2$ | 61.0(0.2) | 61.6(0.4) | 62.9(0.5) | 62.8(0.9) | — | — | 72.5(0.6) | 50.5(0.9) | — | — | — |
| CH$_3$ | 90.1(0.1) | 89.0(0.4) | 88.6(0.4) | 87.5(0.4) | 101.4(0.7) | 76.5(0.5) | 103.5(0.6) | 77.6(0.6) | R | 84.8(0.2) | 84.5(0.4) |
| CH$_3$CH$_2$ | R | 87.9(0.6) | 87.1(0.5) | 85.6(0.6) | 100.0(0.8) | 75.4(0.6) | 102.2(0.7) | 76.7(0.7) | R | 83.3(0.5) | 83.5(0.5) |
| (CH$_3$)$_2$CH | R | R | 85.6(0.5) | 82.7(0.6) | 99.2(0.8) | 75.2(0.7) | 101.0(0.7) | 76.4(0.8) | R | 83.1(0.5) | 81.9(0.5) |
| (CH$_3$)$_3$C | R | R | R | 78.6(0.7) | 97.8(0.8) | 73.2(0.7) | 98.3(0.8) | — | R | — | 79.4(0.6) |
| CH$_2$CH | R | R | R | R | 116(1) | 87.3(0.8) | 116(1) | — | — | — | 41(3)$^a$ |
| CH$_2$CHCH$_2$ | R | R | R | R | R | 62.7(0.6) | — | — | — | — | — |
| HCC | 126.5(0.3) | 125.1(0.5) | 124.5(0.6)$^a$ | 122.3(0.5)$^a$ | — | — | — | — | — | — | — |
| HCC−CH$_2$ | 78(3) | 77(3)$^a$ | — | — | — | — | — | — | — | — | — |
| C$_6$H$_5$ | R | R | R | R | R | — | 118(1) | R | R | 99.3(0.9) | 98.8(0.8) |
| C$_6$H$_5$CH$_2$ | R | R | R | — | — | — | 97(1) | 65.2(0.9) | — | — | 71.4(0.9) |

$^a$ Bond enthalpies of stable organic molecules are tabulated along with their uncertainties. For example, $DH_{298}(C_6H_5-OH) = 112.4 \pm 0.6$ kcal mol$^{-1}$. These bond enthalpies are calculated from the radical heats of formation from Table 1 and the parent $\Delta_f H_{298}$ values tabulated by Pedley et al.[19,20] There are a few entries (such as CH$_3$F or C$_6$H$_5$CH$_2$F) where $\Delta_f H_{298}$(parent) is not provided by Pedley et al., so we have adopted the value recommended by the NIST Web site[46] (http://webbook.nist.gov); we have marked these parent compounds with an "a". In some cases the heat of formation of the parent species is not available (e.g., vinylmethyl ether, CH$_2$CH−OCH$_3$), so the bond enthalpy cannot be computed, and this is marked with a dash. There are a number of redundant entries in this table [e.g., $DH_{298}(C_6H_5-CH_3) = DH_{298}(CH_3-C_6H_5)$], so the second entry is marked with an "R". The uncertainties have been added in quadrature.

**4.**                                                                                (4 min)

Assuming that there are similar concentrations of RH and $Br_2$ in your mechanism for Question 1,  **explain** which radical
should be in higher concentration  Br• or R•.