Chemistry 125 Fifth Examination Answers February 2, 2006 Average Score 71.5; 1/3 > 82; 2/3 > 67

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 4/3 times room temperature.



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.

[Although the R-X bond is established in the lower step, the position of R that forms the new bond is established during H-abstraction, the upper step, because radicals do not rearrange by H-atom migration. Note that we now know that analogous cations do rearrange by hydride shift.]

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)
I here are a number of possible correct answers to this question, because	1	0.00
approximation was encouraged, and because I erroneously had written "1.5 times room	2	0.30
(1) statistical correction by 2/2 for the greater number of primery than according	3	0.48
(1) statistical correction by 3/2 for the greater number of primary than secondary bydrogen atoms (2) relationship of the log of the per-H rate constant ratio to AAH [‡]	4	0.60
and (3) correction for the higher temperature of abstraction by Br.	5	0.70
Hore is how I'd recommend doing it in your head:	6	0.78
	7	0.85
In the first case (chlorination) the ratio of 2° to 1° abstraction rates is $72:28$, but per-	8	0.90
hydrogen it is $72/4$: 28/6, so the ratio of rate constants for H-abstraction is $2.6 \times 3/2 =$	9	0.95
3.9 . The log of this ratio is slightly less than 0.6 (see table).	10	1.00
At room temperature the ratio of rates is about 10 ^{(3/4} $\Delta \Delta H^{a}$),		

i.e. log(ratio) = $3/4 \Delta \Delta H^{\ddagger}$, or $\Delta \Delta H^{\ddagger} = 4/3 \times \log(\text{ratio}) \approx 4/3 \times 0.6 = 0.8 \text{ kcal/mole}$ (precise value 0.79)

In the second case (bromination) the ratio is 98/4: $1.8/6 = 54 \times 3/2 = 81$.

 $log(81) \approx 1.9$ (from table)

The T in the denominator of $\Delta\Delta H^{\ddagger}/RT$ means that instead of $(3/4 \Delta\Delta H^{\ddagger})$ one should have a larger denominator $(3/4 \Delta\Delta H^{\ddagger}) / (4/3)$.

i.e. log(ratio) = 9/16 $\Delta\Delta H^{\ddagger}$, or $\Delta\Delta H^{\ddagger}$ = 16/9 × log(ratio) ≈ 2 × 1.9 = **3.8 kcal/mole** (precise value 3.82)

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.

Table 1 shows that the BDE of ethane is 101.1 kcal/mole, and for the secondary C-H bond of propane is 98.6. Thus if the bonds were completely broken at the transition state for H-abstraction, one would anticipage a $\Delta\Delta H^{\ddagger}$ of 2.5 kcal/mole favoring 2° cleavage.

In the case of abstraction by Br• the new H-Br bond would be worth only 87.5 kcal/mole, so the step is endothermic (uphill) by more than 10 kcal/mole, and one would anticipate a relatively late transition state in which most of the difference between the radicals would appear in the transitions states.

In the case of abstraction by CI• the new H-CI bond would be worth 103.15 kcal/mole, so the step is slightly exothermic (downhill by a few kcal/mole), and one would anticipate a much earlier transition state in which the difference between the radicals would not yet be fully manifest.

As expected the observed difference for Br• (3.82 kcal/mole) is substantially larger than for Cl• (0.79 kcal/mole).

[What might not have been anticipated is that the difference for Br• is **even larger** than was predicted above for *complete* formation of the radicals in the transition state (2.5 kcal/mole). It may be that in the transition state the three electrons involved in bond change (2 in the C-H bond, 1 on the Br atom) spend more time near the more electronegative Br atom than near the C, so that the carbon radical has some special cationic character. Thus the transition state might display something of the much larger difference between 1* and 2* *cations*, rather than the smaller difference between the radical products. One could say that the important resonance structures for the transition state are R-H •Br <-> R• H-Br <-> R+ H• Br . Of course it is not completely obvious why this factor would not also operate with just as much force in the case of abstraction by Cl•]

5. (6 min) Why would one expect to obtain different isomers of butyne after equilibrating with an amide base (like KNHCH₃) than after equilibrating with an alkoxide base (like KOCH₃)?

Short answer: because with the stronger amide base ($pK_a \sim 34$) the most stable species in the equilibrium is the terminal acetylenic anion (*sp vs. sp*³ hybridization for anion, $pK_a = 25$) whereas with the weaker alkoxide base (pK_a 16) the neutral acetylenes predominate, especially the more stable 2-butyne (*sp* C-C vs C-H bonds).

[A fuller explanation is given in frames 14-17 of the Powerpoint for the lecture of 1/30/06]

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

Heating phenylazotriphenylmethane (Ph-N=N-CPh₃) to 100°C in the presence of copper. The Ph• and •CPh₃ radicals couple to give Ph-CPh₃ in miserable yield.

[The reaction was modeled on Thiele's method for preparing the analogous coupling product of two NC-C(CH₃)₂ radicals generated from AIBN. It is not obvious to me that the copper helps this process.]

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?

In free-radical addition the product is selected by adding Br• to form the more stable carbon radical (the more substituted one). This gives the "anti-Markovnikov" product since the Br is attached to the less substituted carbon of the product.

In ionic addition the product is selected by adding H⁺ to form the more stable carbon cation (the more substituted one). This gives the "Markovnikov" product since the Br⁻ attaches to the more substituted carbon of the product.

The $1^{\circ}/2^{\circ}$ difference is more pronounced for the cations than for the radicals.

The two cases share the fact that the more substituted intermediate profits from using sp^2 hybridization in the more-sensitive C-C bonds.

They differ because in the radical case a SOMO mixes with σ HOMO (and σ^* LUMO) in the more substituted isomer, while in the cation case it is an unusually low LUMO (p⁺) that mixes with σ HOMO. The much improved energy-match in the latter case makes the cations more sensitive to substitution than the radicals are.

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.

The R-R' bond dissociation energies span a range of a little less than 12 kcal/mole, hardly larger than the 8.5 kcal/mole range for the corresponding C-H bonds. Much of the instability of the more substituted compounds must come from strain (steric hindrance among methyl groups). When Molecular Mechanics is used to estimate this strain, its range is found to be 10 kcal/mole, almost as large as the range of BDEs.

Thus the strain-corrected C-C bond strengths of R-R' do not show the weakening with substitution that is observed C-H BDEs.

Analogous treatment of the R-OH BDEs shows that the C-O bonds actually get stronger with increasing substitution. This is even true **before** correction for strain energy, which enhances the effect.

9. (6 min) Explain how the "photoelectron spectrum" of the CH₃O⁻ anion allowed accurate determination of the bond dissociation energy of CH₃O-H. It would help to draw an energy diagram.

A good answer to this question must have two parts: (1) explaining how the spectrum gives the electron affinity of CH_3O .

(2) explaining what the electron affinity of CH_3O has to do with determining the BDE of CH_3O -H.

(1) When light whose quanta have the energy 2.540 eV is shone on CH_3O^- in the gas phase, electrons are knocked off and Ellison's task was to measure their kinetic energy, which is the excess of the light energy over the minimum energy required to remove the electron from CH_3O^- (*i.e.* the E.A. of CH_3O^-). Some ejected electrons have less kinetic energy, because some of the excess



energy appears in vibration of CH_3O^- . So one selects the highest (most energetic) peak near 1 eV to subtract from the total light energy (2.450 eV). [The tiny peak at still higher energy is a "hot band" whose extra energy has come from vibration of the initial CH_3O^- .]

(2) Breaking the CH₃O-H bond to give radicals and then removing an electron from H (well known, spectroscopy and quantum mechanics) generates the same species as breaking the bond to ions (gas phase acidity, previously measured by Bierbaum) and then removing an electron from CH₃O⁻.(EA measured by Ellison). That is the sum of BDE and IP must be the same as the sum of Acidity and EA.

Thus subtracting IP from the sum of Acidity and EA gives BDE. [See frames 11 and 12 of 1/11/06 Powerpoint for diagrams]

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.

CH2 CH OCH3

 $\begin{tabular}{ll} & $$ [k_{rel} \ 5 \times 10^{14}]$ \\ Stabilization of secondary cation by $$ resonance.$ (mixing of unshared pair of O with vacant p^+ orbital of secondary cation)$ \end{tabular}$



 $CH_2 = CH_2$

4 [k_{rel} 1] Must form 1° cation, less stable than all the 2° ones.





[k_{rel} 20]

"Inductive" electron withdrawal by Br from C makes this 2° cation harder to form than from propene (but still better than 1° cation from ethylene).

3lanksby and Ellison
Molecules /
of Organic
Energies
Dissociation
Bond

Table 1. Molecular Bond Dissociation Energies for $RH \rightarrow R + H$: Experimental Bond Enthalpies and Radical

		Heats o	f Formation	1 at 298 K			
	<i>DH</i> ₂₉₈ (kcal mol ⁻¹)	$\Delta_{\rm f} H_{298}({ m R})$ (kcal mol ⁻¹)	ref		DH ₂₉₈ (kcal mol ⁻¹)	$\Delta_{\rm f} H_{\rm 298}({ m R})$ (kcal mol ⁻¹)	ref
Hz HF	104.206 ± 0.003 136.25 ± 0.01	52.103 ± 0.003 18.83 ± 0.17	Inorganics 4 6	0H ⁺ → 0 ⁺ + H ⁺	110.21 ± 0.07 115.2 ± 0.1	-33.23 ± 0.07 59.55 ± 0.02	34 34
HCI	103.15 ± 0.03	29.03 ± 0.04	6	H ₂ S	91.2 ± 0.1	34.2 ± 0.2	9
HBr HI	87.54 ± 0.05 71.32 ± 0.06	28.62 ± 0.06 26.04 ± 0.08	00	SH H-NO	84.1 ± 0.2 49.5 ± 0.7	66.2 ± 0.3 21.8 ± 0.1	9 4
H-CN	126.3 ± 0.2	105.0 ± 0.7	9	H-ONO (trans)	79.1 ± 0.2	8.2 ± 0.1	4
NH ₃	107.6 ± 0.1	44.5 ± 0.1	9	H-ONO ₂	101.7 ± 0.4	17.6 ± 0.3	35
H ₂ O OH	118.82 ± 0.07 101.76 ± 0.07	8.86 ± 0.07 59.55 ± 0.02	34 34	SiH4 GeH4	91.7 ± 0.5 83 ± 2	47.9 ± 0.6 53 ± 2	ກດ
			Hvdrocarbon	S			
CH_4	104.99 ± 0.03	35.05 ± 0.07	31	CH ₂ CH-H	110.7 ± 0.6	71.1 ± 0.7	9
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	6	C ₆ H ₅ -H	112.9 ± 0.5	80.5 ± 0.5	9
CH	80.9 ± 0.2	171.3 ± 0.1	6	$C_6H_5 \rightarrow o-C_6H_4 + H$	78 ± 3	106 ± 3	37
CH ₃ CH ₂ -H	101.1 ± 0.4	29.0 ± 0.4	10	$C_6H_5 \rightarrow m - C_6H_4 + H$	94 ± 3	122 ± 3	37
(CH3)2CH-H CH3CH5(CH4)CH-H	98.6 ± 0.4 98.2 ± 0.5	21.5 ± 0.4 16.1 ± 0.5	10	$C_6H_5 \rightarrow p-C_6H_4 + H$ CH_5CHCH_5-H	109 ± 3 88.8 ± 0.4	1.38 ± 3 41.4 ± 0.4	38
(CH ₃) ₃ C-H	96.5 ± 0.4	12.3 ± 0.4	10	C ₆ H ₅ CH ₂ -H	89.8 ± 0.6	49.7 ± 0.6	38
но-на-н	06.1 ± 0.2	-4.08 ± 0.9	Alcohols	н-о-но-но	104.7 ± 0.8	-2 G ± D 8	U U
CH ₂ O-H	104.6 ± 0.7	4.3 ± 0.7	9	(CH ₄) ₅ CHO-H	105.7 ± 0.7	-11.5 ± 0.7	9
CH ₃ S-H	87.4 ± 0.5	29.8 ± 0.4	39,40	(CH ₃) ₃ CO-H	106.3 ± 0.7	-20.5 ± 0.7	9
H-CH ₂ SH	94 ± 2	36 ± 2	39, 40	C ₆ H ₅ O-H	90 ± 3	-58 ± 3	41
Н-ООН	87.8 ± 0.5	3.2 ± 0.5	Peroxides 14	CH3CH200-H	85 ± 2	-6.8 ± 2.3	42
CH300-H	88 ± 1	4.8 ± 1.2	42	(CH ₃) ₃ COO-H	84 ± 2	-25.2 ± 2.3	42
ОНОТН	88 144 ± 0.008	101 ± 01	Carbonyls 6		06 ± 1	-46.5 ± 0.7	45
CH ₃ C(0)-H	89.4 ± 0.3	-2.4 ± 0.3	43	CH3COO-H	112 ± 3	-43 ± 3	44
H-CH ₂ CHO	94 ± 2	2.5 ± 2.2	6	C ₆ H ₅ COO-H	111 ± 4	-12 ± 4	44
HCUU-H	112 ± 5	-30 ± 5	44				

	methyl CH ₃ 104.9(0.1) 115(4) ^a 83.7(0.1) 72.1(0.3) 57.6(0.4) 92.1(0.1) 83.2(0.9) 85.2(0.3) 122.4(0.7) 61.0(0.2)	$\begin{array}{c} {\rm T}\\ {\rm ethyl}\\ {\rm CH_2CH_3}\\ {\rm L01.1(0.4)}\\ -\\ {\rm R4.8(0.5)}\\ 56.9(0.7)\\ 94.0(0.4)\\ 85(1)\\ 84.8(0.4)\\ 85(1)\\ 84.8(0.4)\\ 121.6(0.8)\\ 61.6(1.4)\\ \end{array}$	able 2. Ex isopropyl CH(CH ₃₎₂ 98.6(0.4) 110.6(0.5) 85.2(0.5) 73.9(0.7) 57(1) 95.5(0.4) 85.8(0.5) 86.0(0.4) 120.9(0.5) 62.9(0.5)	perimenta tert-butyl C(CH ₃) ₃ 96.5(0.4) - 84.9(0.7) 72.6(0.6) 55.6(0.9) 95.8(0.4) 84(1) 85.7(0.5) 117.8(0.8) 62.8(0.9)	d Bond E vinyl CHCH ₂ 110.7(0.7) 91.2(0.8) 91.2(0.8) 80.8(0.8) - - 133(1)	$\begin{array}{c} \text{nthalpies, } \\ \text{allyl} \\ \text{CH}_2\text{CHCH}_2 \\ \text{88.8}(0.4) \\ \text{88.8}(0.4) \\ \text{59}(1) \\ \text{45.6}(0.9) \\ \text{80.1}(0.6) \\ \text{20.1}(0.6) \\ \text{108.7}(0.9) \\ \end{array}$	$\begin{array}{c} DH_{298} \ (kc.) \\ Phenyl \\ C_6H_5 \\ 112.9(0.6) \\ 97.1(0.6) \\ 97.1(0.6) \\ 84(1) \\ 67(2) \\ 112.4(0.6) \\ 101(1) \\ 104.2(0.6) \\ 134(1) \\ 72.5(0.6) \end{array}$	$\begin{array}{c c} \textbf{al mol}^{-1} a \\ \below \ benzyl \\ CH_2 C_6 H_5 \\ 89.7 (0.6) \\ 98.7 (0.7)^a \\ 98.7 (0.7)^a \\ 74(1) \\ 51(2) \\ 82.6 (0.7) \\ - \\ 71.7 (0.7) \\ - \\ 71.7 (0.7) \end{array}$	ⁿ methoxy CH ₃ O 104.6(0.7) - 38(1) 42(1)	formyl HC(O) 88.1 (0.2) - - 99.6 (0.9) -	acetyl CH ₃ C(O) 89.4(0.3) 122.2(0.9) 84.7(0.4) 71.7(0.3) 53.8(0.7) 109.9(0.7) 109.9(0.7) 99.1(0.4)
[3 [3CH2 [3CH] [3]3C [3]3C [3]3C [3]2 [3]2 [3]2 [3]2 [3]2 [3]2 [3]2 [3]2	90.1(0.1) R R R R R 126.5(0.3) 78(3)	89.0(0.4) 87.9(0.6) R R R 125.1(0.5) 77(3) ^a	88.6(0.4) 87.1(0.5) 85.6(0.5) R R 124.5(0.6) ^a	87.5(0.4) 85.6(0.6) 82.7(0.6) 78.6(0.7) R R 122.3(0.5) ^a	101.4(0.7) 100.0(0.8) 99.2(0.8) 97.8(0.8) 116(1) R -	76.5(0.5) 75.4(0.6) 75.2(0.7) 73.2(0.7) 87.3(0.8) 62.7(0.6) -	103.5(0.6) 102.2(0.7) 101.0(0.7) 98.3(0.8) 116(1) -	77.6(0.6) 76.7(0.7) 76.4(0.8) - -	22221111	84.8(0.2) 83.3(0.5) 83.1(0.5) - -	84.5(0.4) 83.5(0.5) 81.9(0.5) 79.4(0.6) -
H ₅ H ₅ CH ₂ ^a Bond e kcal mu ulated b we have th an "a" nd enthai [5] = <i>DH</i>	R R nthalpies of ol ⁻¹ . These y Pedley et adopted the adopted the [py cannot be [298(CH ₃ -C ₆]	R stable orga bond entha al. ^{19,20} Thei s value reco ases the he e computed, H ₅]], so the	R R unic molecul uptes are ca re are a few mmended b at of format and this is r second enti	R – es are tabul lculated fro entries (suc y the NIST ion of the p narked with ry is marked	R – m the radio h as CH ₃ F (Web site ⁴⁶ arent speci- a dash. The d with an "1	- with their ur cal heats of or C ₆ H ₅ CH ₂ F (http://webbo es is not ava ere are a num R". The unce	118(1) 97(1) ncertainties formation f β where Δ_{f} ok.nist.gov ilable (e.g., nber of redui	R 65.2(0.9) For exam rom Table ⁷ z98(parent vinylmeth ndant entri ave been a	R – - ple, <i>DH</i> ₂₉₈ (1 and the (1 is not pro marked the marked the vyl ether, C les in this ta dded in qui	 99.3(0.9) - (C₆H₅-OH) parent Δ_f wided by Pe ese parent (H₂CH-OC ible [e.g., Dl adrature. 	98.8(0.8) 71.4(0.9) = $112.4 \pm I_{298}$ values dley et al., compounds H_3), so the $I_{298}(C_6H_5-I_{298})$

Bond Dissociation Energies of Organic Molecules Blanksby and Ellison

Chem 125 Fifth Exam Answers