Organic Structure and Reactivity (CHEM 132-01)

Dr. Fantini

Please do not open until instructed

ALLOWED at exam:
Pens, pencils, erasers.
Calculator

NOT ALLOWED at exam:
Cellular telephones and PDAs

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Examination III   April 26, 2013

Instructions:

1) This exam consists of **7** problems.

2) Work that is not clear and legible will not be graded.

3) Method and/or reasoning must be shown. No credit will be given for an answer alone.

4) Give units for all answers and use significant figures.

5) No books or notes are to be used.

6) Do not share calculators

| Question	Possible	Score
1	15	
2	10	
3	15	
4	20	
5	15	
6	15	
7	10	
TOTAL	100	

Some equations you _might_ use:

Arrhenius equation: $k = Ae^{-Ea/RT}$

Integrated rate laws:

|		
zero-order	$[A]_t = -kt + [A]_o$	$t_{1/2} = [A]_o/2k$
first-order	$ln\ [A]_t = -kt + ln\ [A]_o$	$t_{1/2} = 0.693/k$
second-order	$1/[A]_t = kt + 1/[A]_o$	$t_{1/2} = 1/k[A]_o$

15 1. Shown below is a single stereoisomer of a compound. Please draw all enantiomers and diastereomers for this compound.

Indicate the enantiomeric and diastereomeric relationships among all the stereoisomers. How many stereogenic centers are there?

For each of the stereoisomers, clearly label **R** or **S** at every stereogenic center

To ensure you get the maximum credit, please be sure everything is legible and clearly labeled.
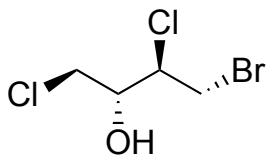
₁₀2. For the following molecules, label the stereocenters as (*R*) or (*S*).
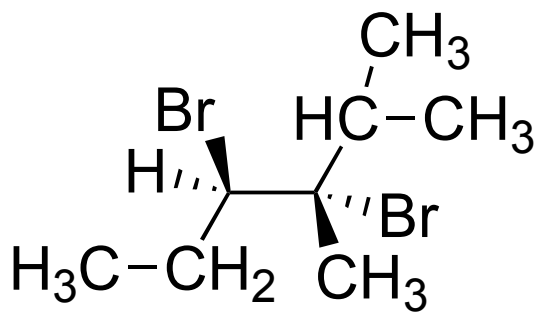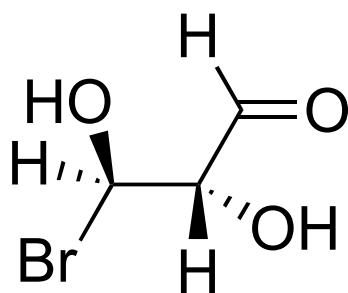
₁₅3. Please draw a Newman projection for the following compound in its **highest-energy conformation** and its **lowest-energy conformation** around the bond indicated in bold and with an arrow. Put the carbon closer to the arrow in front.
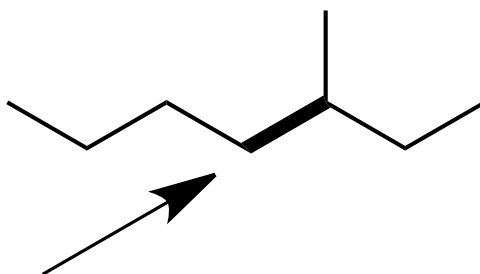

highest-energy conformation	*lowest-energy conformation*

[20]4. The decomposition of $NO_{2(g)}$ at 300 °C was studied by measuring $NO_{2(g)}$ concentration versus time. The following data were obtained for the reaction:

$$NO_{2(g)} \longrightarrow NO_{(g)} + {}^1\!/_2\, O_{2(g)}$$
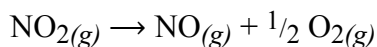
time (s)	[NO$_2$] (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

To determine the order of the reaction you make the following plots: [NO$_2$] vs. t, ln[NO$_2$] vs. t, and 1/[NO$_2$] vs. t. For each graph you ask the computer to do a least squares linear fit to the data. The graphs and equations are shown below.
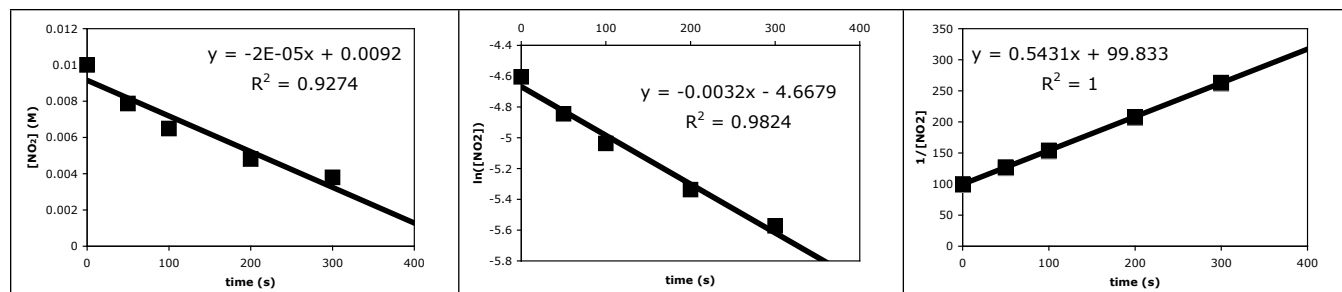
(a) Based on your interpretation of these graphs, is the reaction zero, first, or second order? ***Why?***

(b) Write a rate law for the reaction.

(c) Determine the value of the rate constant k (be sure to use the proper units).

155. Proponents of collision theory explain the temperature dependence of reaction rates by considering the rate constant k to be the product of three factors:

$$k = \mathbf{Zfp}$$

For example, f is the fraction of molecular collisions that occur with enough energy to get over the activation energy barrier from reactants to products ($f = e^{-Ea/RT}$).

(a) In **<u>one sentence each</u>**, give a definition of the terms Z and p.

(b) According to the collision theory of reactions **why** does temperature affect the rate constant (and the rate) of a reaction? **Give the most important factor.** If you discuss more than one factor, be sure to indicate which factor is the most important.

[15]6. When fossil fuels are burned in air, nitric oxide (NO) is formed. Further reaction of nitric oxide with oxygen occurs according to the following equation:

$$2\ NO_{(g)}\ +\ O_{2(g)}\ \longrightarrow\ 2\ NO_{2(g)}$$
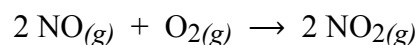
At 25 °C, the following rate data were collected:

| | initial concentrations (M) | | |
Experiment #	[NO]	[O_2]	Initial rate (M/sec)
1	0.0020	0.0010	2.8×10^{-5}
2	0.0040	0.0010	1.1×10^{-4}
3	0.0020	0.0020	5.6×10^{-5}

(a) Determine the rate law for the reaction.

(b) What is the rate constant for this reaction? (be sure to use proper units)

(c) A fourth experiment was conducted for which initial concentrations were [NO] = 0.0125 M and [O_2] = 0.0060 M. What was the initial rate of this reaction?

10 7. For the reaction given below, answer the following questions:

$$5\ Br^-_{(aq)} + BrO_3{}^-_{(aq)} + 6\ H^+_{(aq)} \longrightarrow 3\ Br_{2(aq)} + 3\ H_2O_{(l)}$$
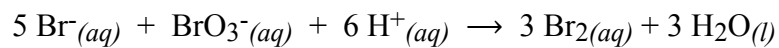
(a)   In words describe how the rate of formation of Br_2 is related to the rate of disappearance of H^+.

(b)   If the rate of appearance of Br_2 is 6.33×10^{-4} M/sec, what is the rate of disappearance of $BrO_3{}^-$?

McQuarrie's Solubility Rules
apply in this order

1. Most alkali metal salts and ammonium salts are soluble.
2. Most nitrates, acetates, and perchlorates are soluble.
3. Most silver, lead, and mercury(I) salts are insoluble.
4. Most chlorides, bromides, and iodides are soluble.
5. Most carbonates, chromates, sulfides, oxides, phosphates, and hydroxides are insoluble, except for hydroxides of Ba^{2+}, Ca^{2+}, and Sr^{2+}, which are slightly soluble.
6. Most sulfates are soluble, except for calcium sulfate and barium sulfate, which are insoluble.

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)						

	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanides	Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0
	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Actinides	Th 232.0	Pa (231)	U 238.0	Np (237)	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (260)