EXAMINATION 1

Chemistry 3A
Professor K. Peter C. Vollhardt
October 3, 1995

Name:_____
[PRINT first name before second. Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

101	Craig Tewell	____	341	Evan Werkema	____
121	Chris Caylor	____	351	Zachary Sweeny	____
131	Jonathan Nitschke	____	361	Heather Wages/ Eugene Chan	____
141	Sarah deForest	____			
151	Paulus Wanandi	____	411	Eric Barchas	____
161	Chloe Laszlo	____	421	Nathanael Gray	____
211	John Robblee	____	431	Hala Gobran	____
221	Joanna Staunton	____	441	Jeff Dysard	____
231	John Cave	____	511	Michael Furlanetto	____
311	Robin Fulton	____	521	Scott Andryski	____
321	Jeff Golden	____	531	Ryan Bise	____
331	Marcel Bruchez	____	541	Kenneth Kotz	____

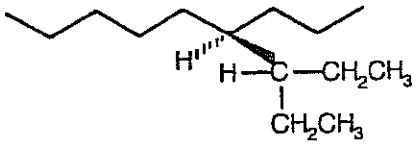
Making up an I grade ____
(If you are, please indicate the semester during which you took Chem 3A previously _____)

Please write the answers you want graded in the spaces provided. Do scratch work on the backs of the pages. This exam should have 13 numbered pages. Check to make sure that you have received a complete exam. A few good pieces of advice: **read carefully over the questions at least twice; make sure that you understand exactly what is being asked; avoid sloppy structures or phrases, it is better to be pedantic in accuracy! Good luck!**

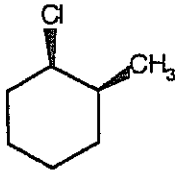
I	_____	(30)
II	_____	(20)
III	_____	(30)
IV	_____	(20)
V	_____	(50)
VI	_____	(30)
VII	_____	(10)
VIII	_____	(10)
TOTAL		(200)

I. [30 points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis, trans* or *R, S, meso*)

a)



b)



racemic

c)

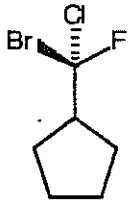
(2R)-Bromo-1,1-dimethyl-cycloheptane

d)

Meso-3,6-bis(cyclopropyl)octane

(Fischer projection)

e)



11. [20 Points] Write the most favorable Lewis *octet* structure for each of the molecules depicted below (don't forget formal charges).

a) HCNO (Cyanic acid):

H C N O

b) ClO_2^- (Chlorite ion):

O Cl O

c) N_2O_3 (Dinitrogen trioxide):

O
O N N
O

d) $[CH_2CO_2]^{2-}$ (Acetic acid dianion):

H O
C C
H O

III. [30 Points] George Olah (University of Southern California; Nobel Prize 1994) showed that in highly acidic media, methane can be protonated to the methonium ion CH_5^+. This species is also formed on treatment of CH_3^+ with H_2, in a remarkably exothermic reaction:

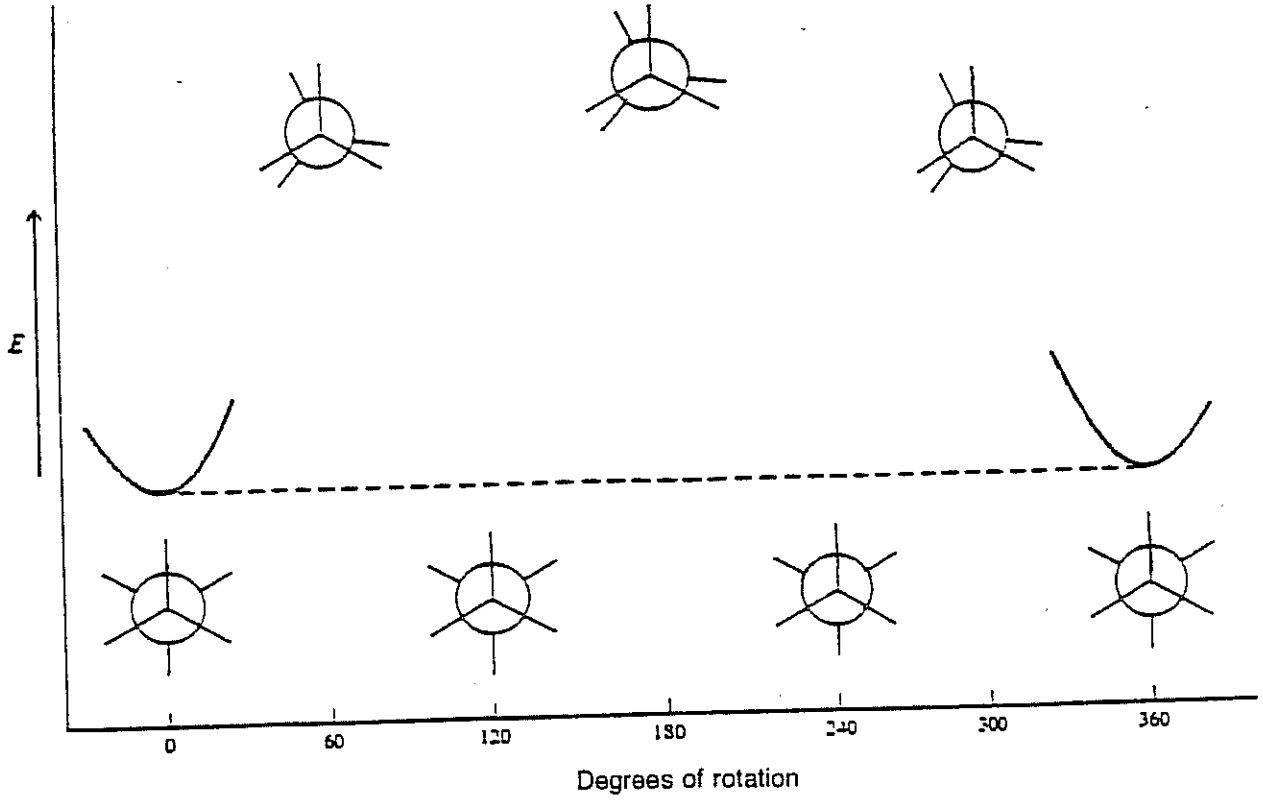
$$CH_3^+ + H_2 \longrightarrow CH_5^+ \qquad \Delta H^\circ = -40 \text{ kcal mol}^{-1}$$

a) Depict the molecular orbitals of CH_3^+, clearly labeling the hybrids on each carbon, the atomic orbital of the hydrogens, and the location of the charge.

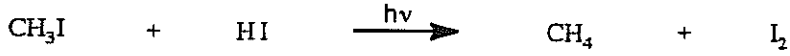
b) Draw the energy diagram for the formation of CH_5^+ by the reaction of CH_3^+ with H_2. Clearly depict the energy levels of the orbitals entering into overlap and label them, and show the resulting bonding and antibonding molecular orbitals. Place the relevant electrons into the various levels.

c) The ΔG° for the reaction in (b) is about - 33 kcal mol^{-1}. Why is this value less negative than that of ΔH°? Write the relevant thermodynamic equation relating ΔG° to ΔH°.

IV. [20 Points] Draw a potential energy diagram describing the rotation around the C1-C2 bond(underlined carbons) in 1-methoxypropane, $CH_3O\underline{C}H_2\underline{C}H_2CH_3$, using the stencil given below. Complete the Newman projections starting with the most stable rotamer at 0°. Indicate gauche and anti forms, transition states, and the relative positions of the maxima and minima of the curve. Note: the top three Newman projections are eclipsed forms.



V. [50 Points] Iodomethane reacts with hydrogen iodide under free radical conditions (hν) to give methane and iodine:



a) Write a mechanism for this reaction including initiation, propagation, and (one) termination steps.

Initiation:

Propagation:

Termination:

b) The bond strength in iodine is 36 kcal mole^{-1} and other relevant DH$^{\circ}$ values can be obtained from the following table:

TABLE 3-1 **Bond-Dissociation Energies of Various A–B Bonds (DH° in kcal mol^{-1})**

	B in A–B							
A in A–B	–H	–F	–Cl	–Br	–I	–OH	$-NH_2$	$-CH_3$
H—	104	135	103	87	71	119	107	105
CH_3—	105	110	85	71	57	93	80	90
CH_3CH_2—	98	107	80	68	53	92	77	86
$CH_3CH_2CH_2$—	98	107	81	68	53	91	78	87
$(CH_3)_2CH$—	94.5	106	81	68	53	92	93	86
$(CH_3)_3C$—	93	110	81	67	52	93	93	84

Calculate the enthalpies (ΔH°) of the overall transformation and of all the mechanistic steps. Show your work.

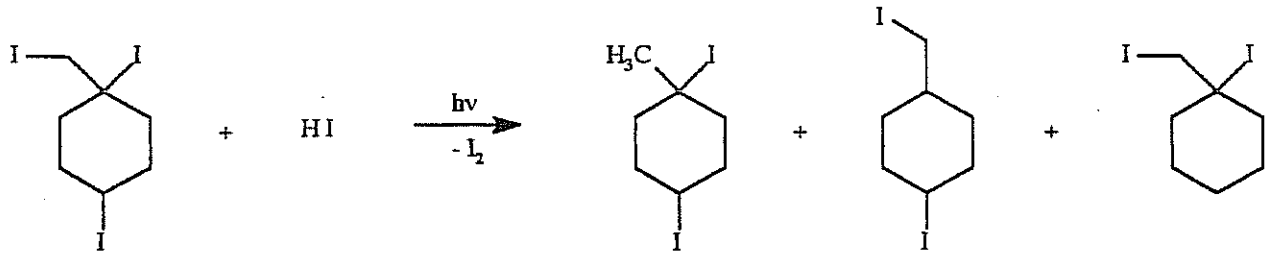
ΔH° of overall reaction:

ΔH° of initiation:

ΔH°s of propagation steps:

ΔH° of your termination step:

c) The same reaction of HI with 1,4-diiodo-1-(iodomethyl)cyclohexane (**A**) gave the following product distribution:



A 1 : 100 : 10

What is the relative reactivity for iodine abstraction by the iodine atom?

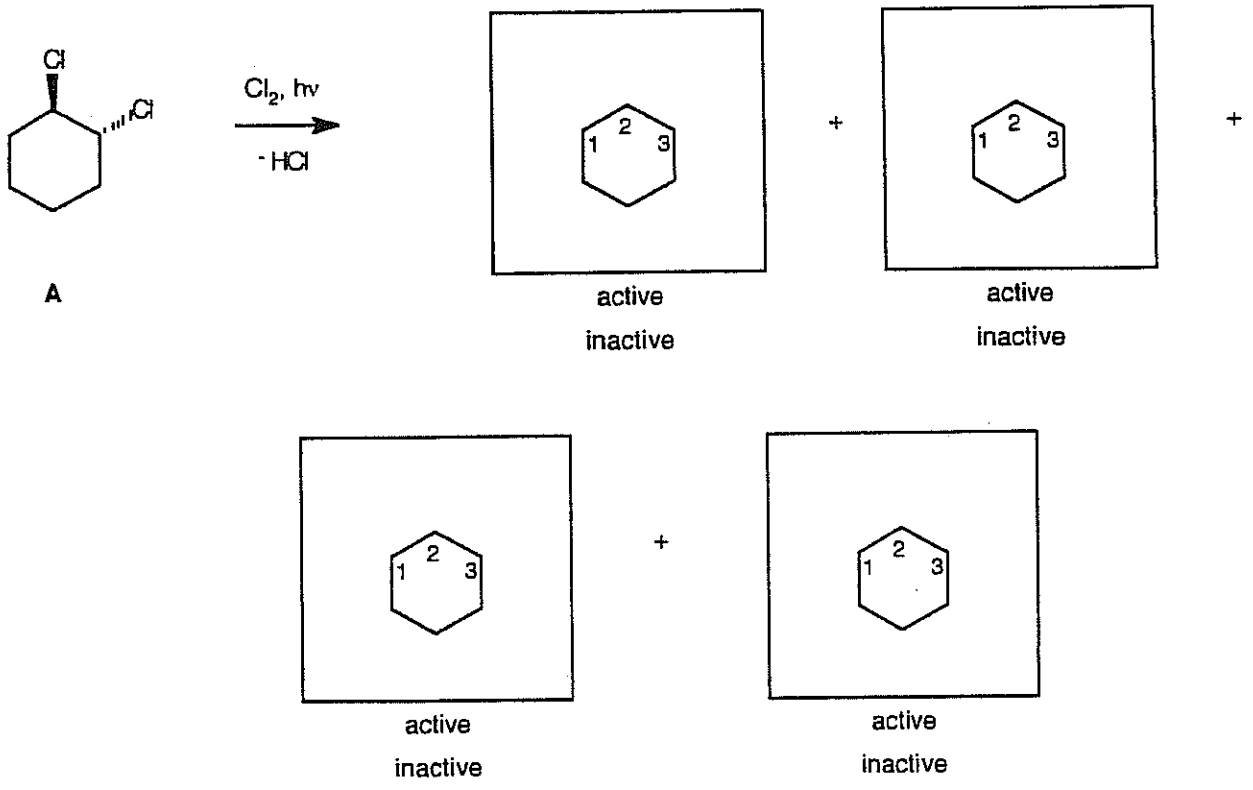
$I_{primary} : I_{secondary} : I_{tertiary}$ =

d) The experimental heats of formation of the components in the reaction of CH_3I with HI are given below:

ΔH_f° (gas): CH_3I 3.5 HI 6.3 CH_4 -17.9 I_2 15 kcal mol^{-1}.

Calculate again the ΔH° of the reaction. Show your work.

VI. [30 Points] Free radical chlorination of optically active *trans*-1,2-dichlorocyclohexane (A) gave more than one (but fewer than five) 1,2,3-trichlorocyclohexanes (among other chlorinated products).



a) Draw the products using the flat stencils provided above. Note: the four boxes shown may be in excess of what you need. Clearly label each product as optically active or optically inactive by circling the appropriate descriptor.

b) The energy difference between axial and equatorial chlorocyclohexane is 0.52 kcal mol^{-1}. Using the chair cyclohexane stencils on the following page (with the numbering shown) draw the two conformers for each of the answers given in part (a). Label the most stable compound in each pair and the ΔG° for ring flip. Note: again you may not need all of the equations shown.

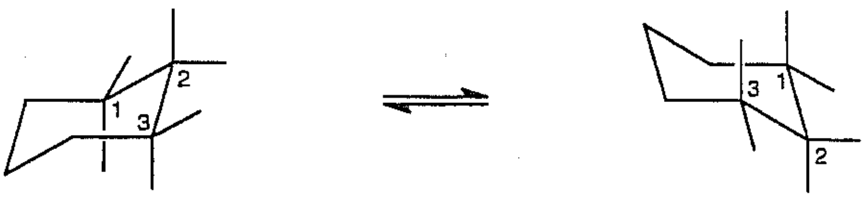
see next page

Answer for VI (b):

ΔG° =

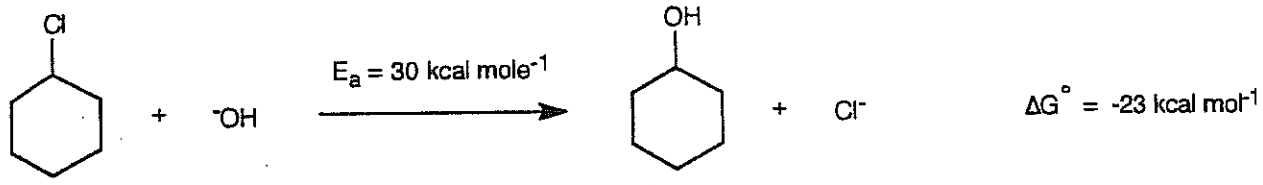
ΔG° =

ΔG° =

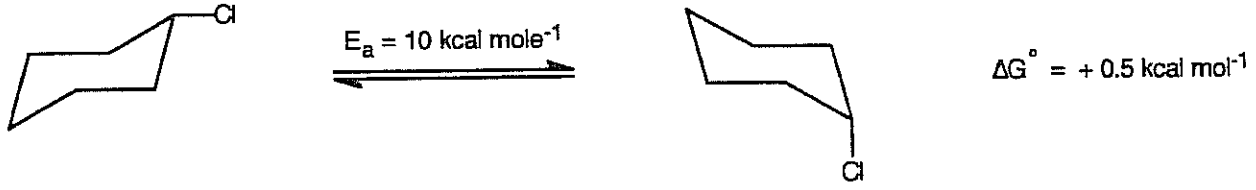


ΔG° =

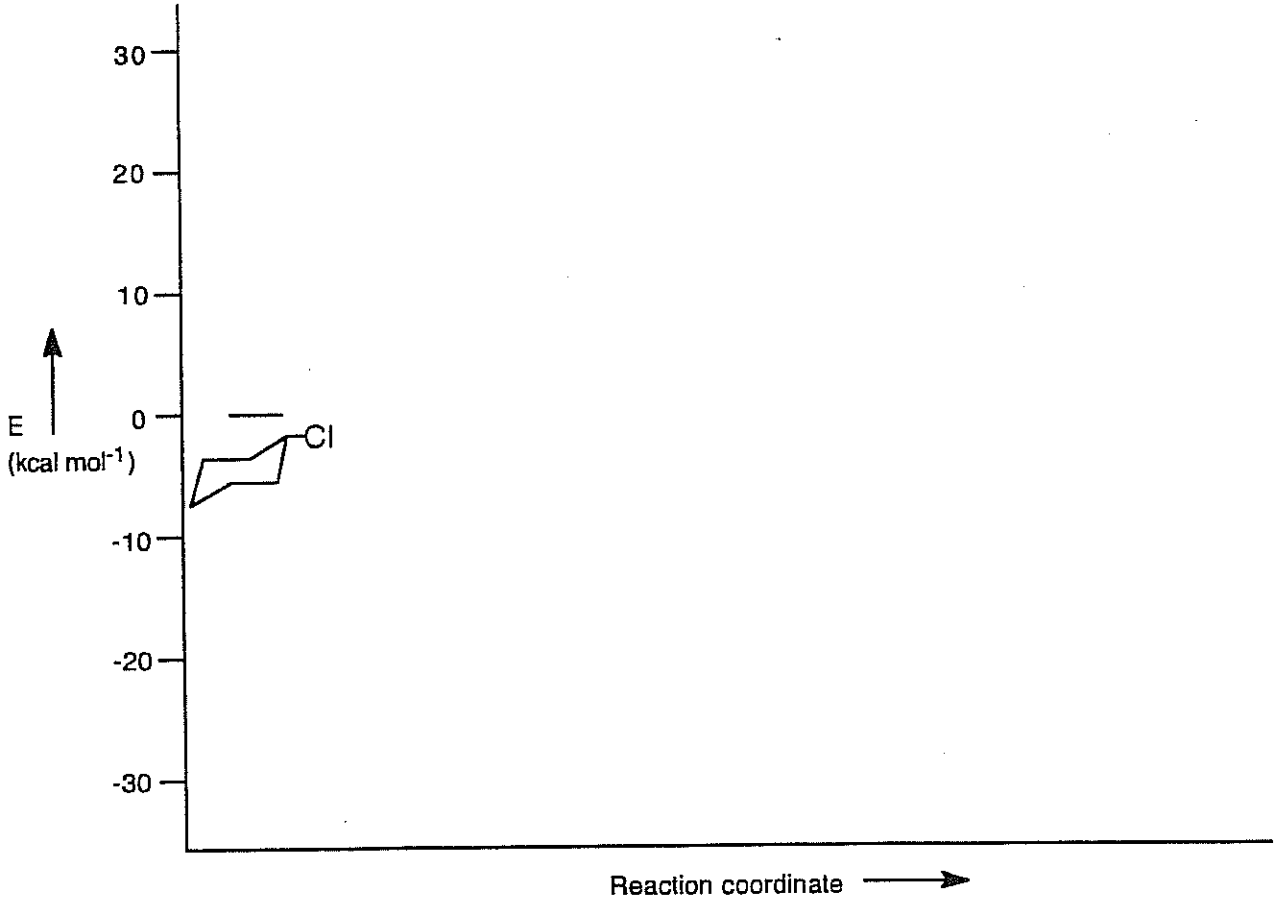
VII [10 Points] Chlorocyclohexane reacts with hydroxide ion to form cyclohexanol as shown.



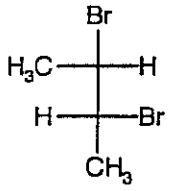
The reaction follows second order kinetics and proceeds through the axial form of chlorocyclohexane. Thus the equilibrium below precedes the hydroxide attack above:

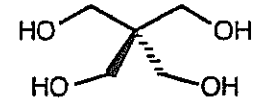


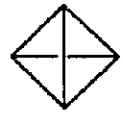
Draw a potential energy diagram for the overall process, starting with equatorial chlorocyclohexane (arbitrarily assigned relative energy = 0) and ending with cyclohexanol. Show (qualitatively) the relative energies of starting material, intermediate, products, and transition states. Label the rate-determining transition state and fill in the E_a and ΔG° values given where appropriate.

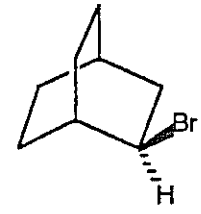


V I I I [10 Points] Label (in the boxes provided) each of the following molecules as chiral (c) or achiral (a).









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