MAD ORG. CHEM. MIN. # 11

LAST NAME____________________ FIRST NAME____________________

ID#____________________ CIRCLE CLASS TIME: 10AM 1 PM

1°C 1°C

1. For the following reaction, calculate ΔH° and label as exothermic or endothermic. Does the equilibrium lie to the left or right?

$$\xrightarrow{EQ}$$

$$CH_3CH_3 + Br_2 \rightleftarrows CH_3CH_2Br + HBr$$

98 Kcal/mol 46 Kcal/mol 68 Kcal/mol 88 Kcal/mol

$$\Delta H^\circ = \Sigma \text{ bonds broken} - \Sigma \text{ bonds formed}$$

$$= (98 + 46) - (68 + 88)$$

$$= -12 \text{ kcal/mol} \leftarrow \underline{\underline{\text{exo}}}$$

, EQ lies to (R)
products formed

TABLE 4-2 Bond-Dissociation Energies for Homolytic Cleavages

$$A{:}B \longrightarrow A\cdot + \cdot B$$

Bond	Bond-Dissociation Energy kcal/mol
H—X bonds and X—X bonds	
H—H	104
D—D	106
F—F	38
Cl—Cl	58
Br—Br	46
I—I	36
H—F	136
H—Cl	103
H—Br	88
H—I	71
HO—H	119
HO—OH	51
Methyl bonds	
CH_3—H	104 ← No!
CH_3—F	109
CH_3—Cl	84
CH_3—Br	70 ← No!
CH_3—I	56
CH_3—OH	91
Bonds to primary carbons	
CH_3CH_2—H	98
CH_3CH_2—F	107
CH_3CH_2—Cl	81
CH_3CH_2—Br	68
CH_3CH_2—I	53
CH_3CH_2—OH	91
$CH_3CH_2CH_2$—H	98
$CH_3CH_2CH_2$—F	107
$CH_3CH_2CH_2$—Cl	81
$CH_3CH_2CH_2$—Br	68
$CH_3CH_2CH_2$—I	53
$CH_3CH_2CH_2$—OH	91

Bond		Bond-Dissociation Energy kcal/mol
Bonds to secondary carbons		
$(CH_3)_2CH$—H		95
$(CH_3)_2CH$—F		106
$(CH_3)_2CH$—Cl		80
$(CH_3)_2CH$—Br		68
$(CH_3)_2CH$—I		53
$(CH_3)_2CH$—OH		91
Bonds to tertiary carbons		
$(CH_3)_3C$—H		91
$(CH_3)_3C$—F		106
$(CH_3)_3C$—Cl		79
$(CH_3)_3C$—Br		65
$(CH_3)_3C$—I		50
$(CH_3)_3C$—OH		91
Other C—H bonds		
$PhCH_2$—H	(benzylic)	85
CH_2=$CHCH_2$—H	(allylic)	87
CH_2=CH—H	(vinyl)	108
Ph—H	(aromatic)	110
$\boxed{\text{C—C bonds}}$		
CH_3—CH_3		88 ← No
CH_3CH_2—CH_3		85
CH_3CH_2—CH_2CH_3		82
$(CH_3)_2CH$—CH_3		84
$(CH_3)_3C$—CH_3		81
CH_2=$CHCH_2$—Br	(allylic Br)	85

MAD ORG. CHEM. MIN. # 11b

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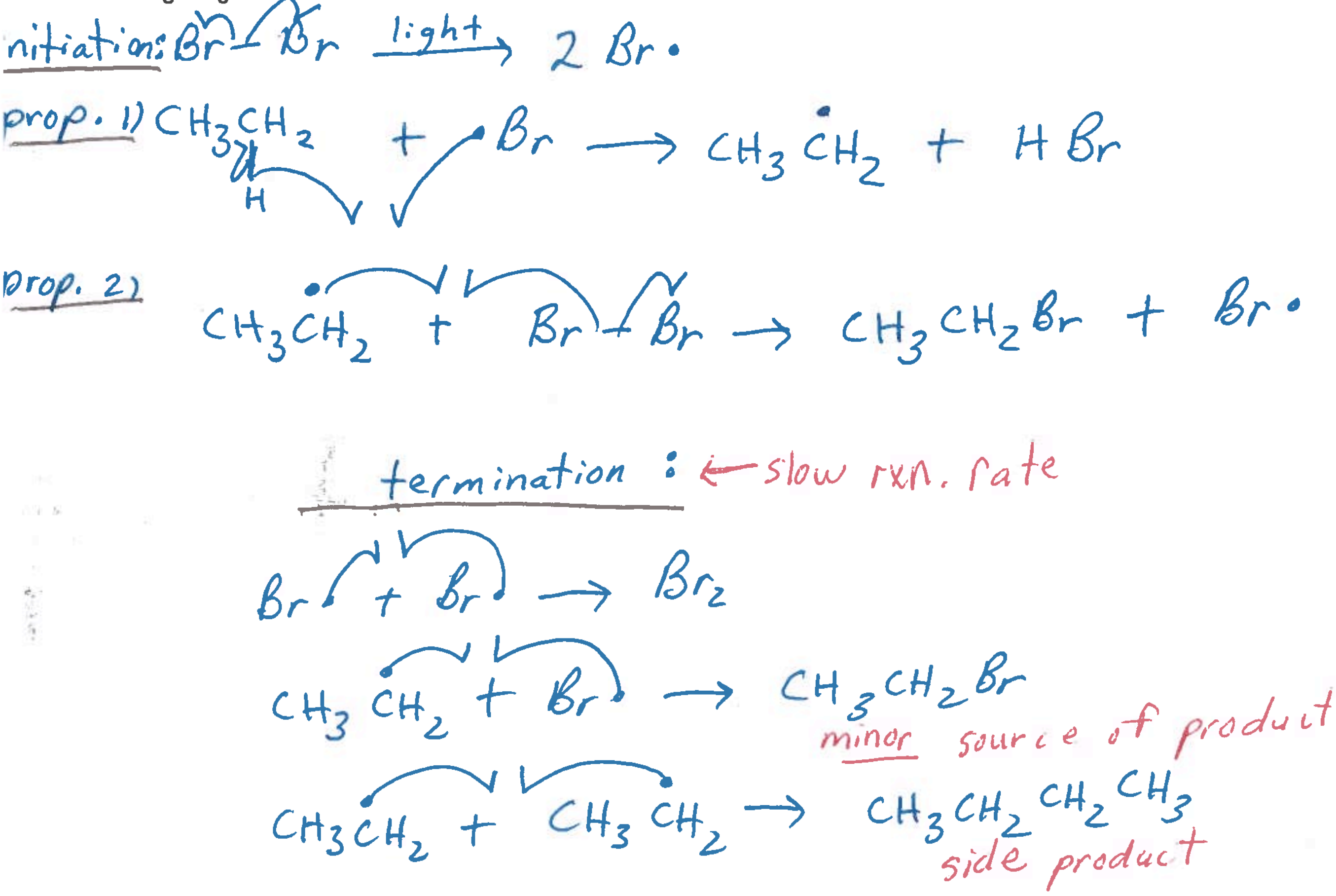
PSID #____________________ CIRCLE CLASS TIME: 10AM 1PM

Write a detailed mechanism for the reaction below.

$$CH_3CH_3 + Br_2 \xrightarrow{\text{light}} CH_3CH_2Br + HBr$$



nitiation: $Br{-}Br \xrightarrow{\text{light}} 2\ Br\cdot$

prop. 1) $CH_3CH_2{-}H + \cdot Br \rightarrow CH_3\dot{C}H_2 + HBr$

prop. 2) $CH_3\dot{C}H_2 + Br{-}Br \rightarrow CH_3CH_2Br + Br\cdot$

termination : ← slow rxn. rate

$Br\cdot + Br\cdot \rightarrow Br_2$

$CH_3\dot{C}H_2 + Br\cdot \rightarrow CH_3CH_2Br$ minor source of product

$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \rightarrow CH_3CH_2CH_2CH_3$ side product

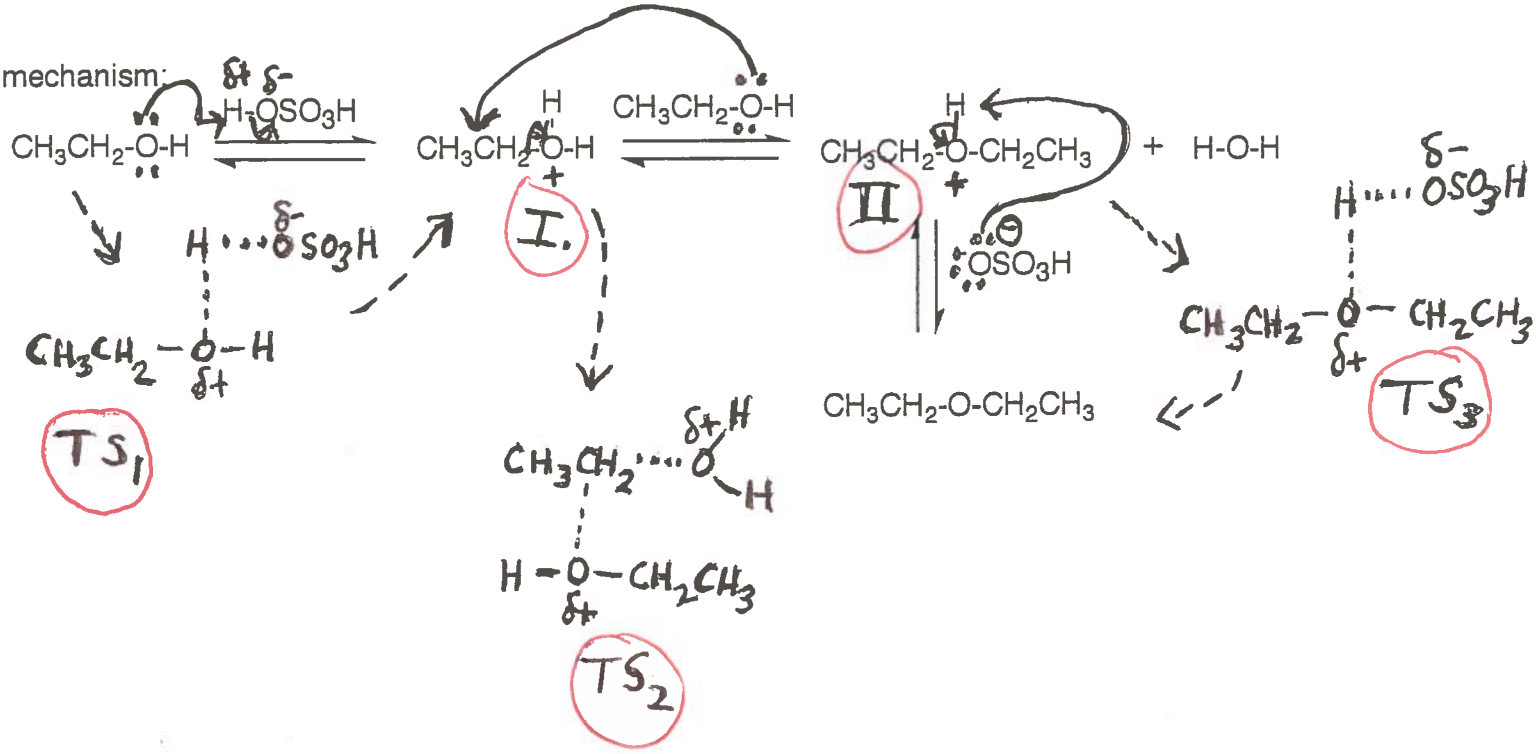
MAD ORG. CHEM. MIN. # 11b

LAST NAME____________________ FIRST NAME____________________

SS#____________________ CIRCLE CLASS TIME: 10AM 5:30PM

1. An industrial synthesis of diethyl ether involves the high temperature, acid catalyzed condensation of two ethanol molecules. This process is shown below. Draw all of the transition states and label the intermediates (I, II, III, etc.).

reaction: $CH_3CH_2OH + CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$



b) Assuming that this process is exothermic overall, and that step 2 is the rate determining step and step 1 is faster than step 3, draw an enerygy profile for this process.