

Unit 5 - Week 4

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Lecture 16 : Scales used in Hammett Plots

Lecture 17 : Deviation from Linear Free Energy Relationships

Lecture 18 : LFER for Sterics: The Taft Parameters

Lecture 19 : Solvent Effects: Part A

Quiz : Assignment 4

Assignment 4 solutions

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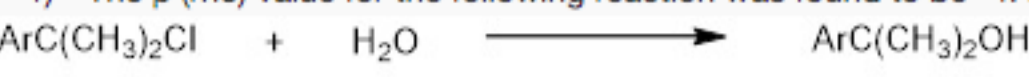
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Assignment 4

The due date for submitting this assignment has passed.
As per our records you have not submitted this assignment.

Due on 2019-08-28, 23:59 IST.

1) The ρ (rho) value for the following reaction was found to be -4.48. Which of the following statements is/are correct for this reaction? **1 point**



- The reaction follows an $\text{S}_{\text{N}}1$ mechanism
 The reaction follows an $\text{S}_{\text{N}}2$ mechanism
 The reaction rate will significantly increase with increase in solvent polarity.
 The reaction rate will not change with an increase in solvent polarity
 The reaction rate will decrease with increase in solvent polarity.

No, the answer is incorrect.
Score: 0

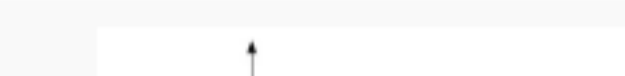
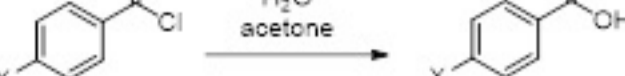
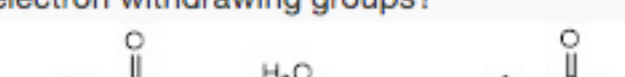
Accepted Answers:

The reaction follows an $\text{S}_{\text{N}}1$ mechanism
 The reaction rate will significantly increase with increase in solvent polarity.

2) Which of the following plots represents the hydrolysis of ArCOCl (A), given that the reaction constant = -4.4 for electron releasing groups and +2.5 for electron withdrawing groups? **1 point**



A



No, the answer is incorrect.
Score: 0

Accepted Answers:



3) Given that the ρ (rho) value for the benzoate for para substituted aniline (B) is -2.69, the rate determining step is **1 point**



B

- step a
 step b
 step c

No, the answer is incorrect.
Score: 0

Accepted Answers:

step a

4) Which LFER parameter would best represent the following reaction? **1 point**



- σ^+
 σ^-
 σ

No, the answer is incorrect.
Score: 0

Accepted Answers:

σ^+

5) For the reaction given, the plot of $k_{\text{azide}}/k_{\text{solvent}}$ against σ^+ (sigma +) has a negative slope (large magnitude) for electron releasing substituents and a positive slope (<1) for electron withdrawing substituents. Such a plot is seen because **1 point**



- The mechanism is $\text{S}_{\text{N}}2$ for highly electron withdrawing substituents and $\text{S}_{\text{N}}1$ for highly electron releasing substituents.
 The reaction mechanism is $\text{S}_{\text{N}}1$, but the rate determining step is different for electron withdrawing and electron releasing substituents.
 The mechanism is $\text{S}_{\text{N}}1$ for highly electron withdrawing substituents and $\text{S}_{\text{N}}2$ for highly electron releasing substituents.
 The reaction mechanism is $\text{S}_{\text{N}}2$, but the rate determining step changes for electron withdrawing and electron releasing substituents.

No, the answer is incorrect.
Score: 0

Accepted Answers:

The mechanism is $\text{S}_{\text{N}}2$ for highly electron withdrawing substituents and $\text{S}_{\text{N}}1$ for highly electron releasing substituents.

6) Based on the information provided about sign of ρ (rho) for the two reactions given below, one can conclude that **1 point**

Reaction A: Negative rho value



Reaction B: Positive rho value



- Reaction A: Carbene acts as a nucleophile; Reaction B: Carbene acts as an electrophile
 Reaction A: Carbene acts as an electrophile; Reaction B: Carbene acts as a nucleophile
 Carbene acts as a nucleophile in both reactions
 Carbene acts as an electrophile in both reactions

No, the answer is incorrect.
Score: 0

Accepted Answers:

Reaction A: Carbene acts as a electrophile; Reaction B: Carbene acts as a nucleophile

7) Match the R groups in Column P to the Taft parameter (E_s) in Column Q. **1 point**

i	P	a	Q
ii	i-Pr	b	-0.47
iii	t-Bu	c	-2.55
iv	Ph	d	-1.54

- i-b, ii-a, iii-d, iv-c
 i-c, ii-b, iii-c, iv-d
 i-c, ii-a, iii-b, iv-d
 i-b, ii-a, iii-c, iv-d

No, the answer is incorrect.
Score: 0

Accepted Answers:

i-b, ii-a, iii-d, iv-c

8) The standard reaction for determining the Taft parameters for sterics is **1 point**

- Hydrolysis of methyl acetate.
 Hydrolysis of methyl formate.
 Hydrolysis of methyl benzoate.
 Dissociation of benzoic acid
 Dissociation of phenol

No, the answer is incorrect.
Score: 0

Accepted Answers:

Hydrolysis of methyl acetate.

9) Match the reactions given in Column L to the solvent effect given in Column M **1 point**

Column L: Reaction	Column M: Effect on increasing solvent polarity
i $\text{CH}_3\text{CH}_2\text{S}^{\ominus}(\text{CH}_3)_2 + \text{OH}^{\ominus} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{S}^{\ominus}(\text{CH}_3)_2$	a increase in rate
ii $\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Br}^{\ominus}$	b decrease in rate
iii $\text{Cyclohexene} + \text{R}^{\oplus} \longrightarrow \text{Cyclohexane-R}$	c Negligible change in rate
iv $\text{Cyclohexane-Cl} + \text{H}_2\text{O} \longrightarrow \text{Cyclohexane-OH}$	

- i-b, ii-a, iii-c, iv-a
 i-a, ii-b, iii-c, iv-b
 i-b, ii-c, iii-c, iv-a
 i-a, ii-c, iii-c, iv-b

No, the answer is incorrect.
Score: 0

Accepted Answers:

i-b, ii-a, iii-c, iv-a

10) For the bimolecular reaction of 2-bromopropane in aqueous ethanol of reaction I with OH^{\ominus} as nucleophile: The rate constant decreases by a factor of 1.6 when the proportion of water was raised from 20% to 40%. Reaction II with water as nucleophile: The rate constant increases by a factor of 2.8 when the proportion of water was raised from 20% to 40%. These observations can be explained by the fact that **1 point**

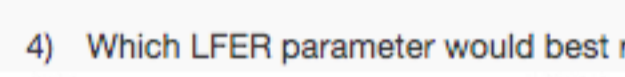
- Water stabilizes reactant more than transition state in reaction I.
 Water stabilizes reactant more than transition state in reaction II
 Water stabilizes transition state more than reactant in reaction I
 Water stabilizes transition state more than reactant in reaction II

No, the answer is incorrect.
Score: 0

Accepted Answers:

Water stabilizes reactant more than transition state in reaction I.
 Water stabilizes transition state more than reactant in reaction II

11) The equilibrium constant for the reaction given below will be maximum in **1 point**



- Gas phase
 Water
 Acetonitrile
 Chloroform

No, the answer is incorrect.
Score: 0

Accepted Answers:

Gas phase

12) Which of the following statements is true for the reaction given below? **1 point**



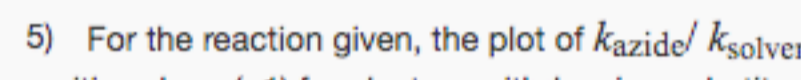
- The reaction has a positive rho (ρ) value, if the substituent at the aromatic ring is varied.
 The reaction has a negative rho (ρ) value, if the substituent at the aromatic ring is varied.
 The reaction rate will increase when the substituent is changed from NHCOCH_3 to OMe
 The reaction rate will increase when the substituent is changed from NHCOCH_3 to CN .

No, the answer is incorrect.
Score: 0

Accepted Answers:

The reaction has a negative rho (ρ) value, if the substituent at the aromatic ring is varied.
 The reaction rate will increase when the substituent is changed from NHCOCH_3 to OMe

13) Calculate the rate constant (of the order of $10^{-4} \text{ M}^{-1}\text{s}^{-1}$) for the following reaction given that the rate of hydrolysis of methylbenzoate is $2 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, $\sigma_{\text{m}}(\text{NO}_2)$ is 0.70, $\sigma_{\text{p}}(\text{NO}_2)$ is 0.778 and ρ (rho) is 2.38 **1 point**



Hint

No, the answer is incorrect.
Score: 0

Accepted Answers:

(Type: Range) 92,94