Seoul National University
457.620.001
Water Contaminants

FINAL EXAMINATION - SOLUTIONS

TIME ALLOWED: 75 MINUTES

June 04, 2020

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1. Students may use two double-sided, A4 notes prepared in their own handwriting. Mechanical or electronic reproduction of any notes are not allowed.

2. Students should bring their own calculator which is not pre-programmed with formulae from the class.

3. Be aware that the cheated student will get 80% of the lowest score in class! There is no tolerance at all.

4. Make sure your answers include units if appropriate. Watch your units! Prepare your answers in a logical, easy-to-follow format.

1. Mark O or X for the following statements.

(+2 points for correct answers; -2 points for incorrect answers)

1) Ca^{2+} ion in a water sample with an ionic strength of 10^{-2} has a smaller activity coefficient value than that of Na^{+} ion in the same water sample.

Answer) O

2) The COD/TOC ratio of acetic acid (CH_3COOH) is smaller than the COD/TOC ratio of ethanol (C_2H_5OH).

Answer) O

3) Toluene ($C_6H_5CH_3$) is a planar molecule.

Answer) O

4) 1,3-butadiene (C_4H_6) has a conjugated double bond.

Answer) O

5) Persistent organic pollutants are often used as conservative tracers.

Answer) X

6) Reductive dechlorination of trichloroethene occurs at an appreciable rate (half life in the order of months) abiotically in the dark in the absence of catalysts.

Answer) X

7) Transformation of a molecule structure always occur if the molecule absorbs a photon with sufficient energy to induce the transformation.

Answer) X

8) The resistance at the gas phase boundary layer dominates the overall resistance of mass transfer at the air-water interface for highly volatile compounds.

Answer) X

9) The greater the Peclet number, the more dominant the dispersion over advection.

Answer) X

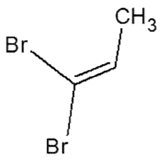
10) For rivers, the overall dispersion coefficient in the longitudinal direction is typically much smaller than the overall dispersion coefficient in the vertical direction.

Answer) X

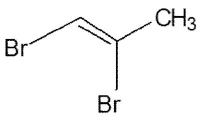
2. For a compound represented by a molecular formula of $C_3H_4Br_2$, answer the followings.

1) Provide all possible structures (i.e., constitutions) and indicate the systematic names for each. (8 points)

Answer)

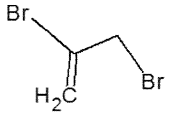


1,1-dibromopropene



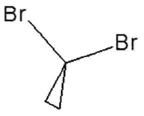
1,2-dibromopropene

1,3-dibromopropene

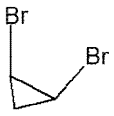


2,3-dibromopropene

3,3-dibromopropene



1,1-dibromocyclopentane

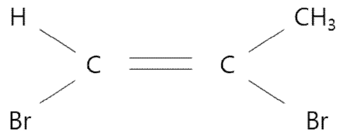


1,2-dibromocyclopentane

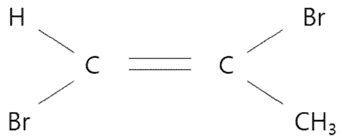
2) Does any of the structural isomers have a pair of stereoisomers? If yes, provide the geometry of the stereoisomeric compounds. (6 points)

Answer)

i) 1,2-dibromopropene

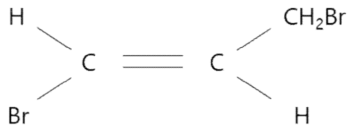


cis-1,2-dibromopropene

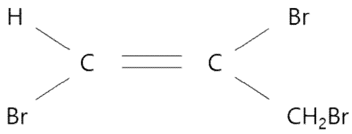


trans-1,2-dibromopropene

ii) 1,3-dibromopropene



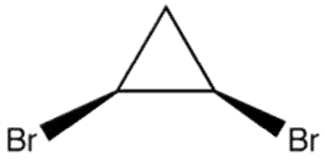
cis-1,3-dibromopropene



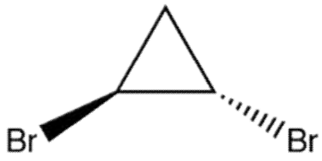
trans-1,3-dibromopropene

iii) 1,2-dibromocyclopentane

cis–1,2–dibromo
cyclopropane **(1)**

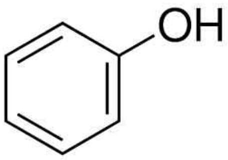


trans–1,2–dibromo
cyclopropane **(2)**

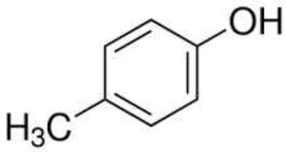


3. Compare the pK_a values of the compounds given below. Explain your rationale. (9 points)

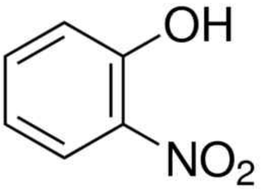
phenol



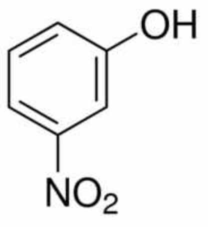
p-cresol



2-nitrophenol



3-nitrophenol



Answer)

CH_3 – electron donating group; NO_2 – electron withdrawing group

→ So, deprotonated form of p-cresol should be less stable than phenolate (deprotonated phenol) while deprotonated form of nitrobenzenes should be more stable.

Electron withdrawing property will be more pronounced if the group is attached at ortho- or para- position.

→ So, deprotonated form of 2-nitrobenzene should be more stable than deprotonated form of 3-nitrobenzene.

More stable when deprotonated → lower pK_a

∴ pK_a should be in the order of: 2-nitrobenzene < 3-nitrobenzene < phenol < p-cresol

** literature pK_a values*

2-nitrobenzene: 7.2 / 3-nitrobenzene: 8.4 / phenol: 10.0 / p-cresol: 10.3

4. Compound A is being chemically reacted to generate a final product C. As shown in the following, the reaction occurs in two steps that are in series. Both steps are irreversible and are expressed as a first-order reaction with rate constants k_1 and k_2.

Step 1: $A \xrightarrow{k_1} B$ $\quad k_1 = 100\, day^{-1}$

Step 2: $B \xrightarrow{k_2} C$ $\quad k_2 = 0.1\, day^{-1}$

The initial concentrations for the compounds are as follows:

$[A]_0 = 5\,mM \qquad [B]_0 = 3\,mM \qquad [C]_0 = 2\,mM$

Calculate the concentration of B after 2 days. (10 points)

Answer)

Step 2 is the rate-controlling step, and because $k_1 \gg k_2$ *and* $t_{1/2} = \ln 2/k_1 = 6.93 \times 10^{-3}\,day$*, compound A will be readily converted to B at the very initial phase of the reaction. So, in a time scale of 2 days, this reaction can be simplified as the following single step reaction:*

$$B \xrightarrow{k_o} C \qquad k_o \approx 0.1\,day^{-1},\ [B]_0 \approx 8\,mM$$

Then,

$$[B] = [B]_0 \exp(-k_o t) = 8 \cdot \exp(-0.1 \cdot 2) = 6.55\ mM$$

5. Determine the pH at which the hydrolysis rate of CH_3Br with H_2O as a reactant and the hydrolysis rate of CH_3Br with OH^- as a reactant are identical, in other words, the I_{NB} value for the hydrolysis of CH_3Br. Assume molarity = activity, temperature = 25 ℃, and use $n_{OH^-,CH_3Br} = 4.2$. (10 points)

Answer)

$$[OH^-]_{50\%} = 55.3 \times 10^{-n_{OH^-,CH_3Br}} = 55.3 \times 10^{-4.2} = 3.49 \times 10^{-3}\,M$$

This is the [OH⁻] concentration at which the reaction rates with H_2O *and* OH^- *are identical. Thus,*

$$I_{NB} = 14 + \log[OH^-]_{50\%} = 11.5$$

6. Plumlee & Reinhard (2007) reported the overall specific light absorption rate of 0.12~0.24 einstein/mole-hr for n-dimethylnitrosanmine (NDMA) in a natural river with 1 m mixed water depth under midday solar irradiance condition of Southern California, USA. They also reported a reaction quantum yield value of 0.41 for NDMA.

The second-order rate constant for reaction between hydroxy radical (·OH) and NDMA is reported as 4.0×10^{8} L/mole-s in the literature. In addition, Brezonik & Fulkerson-Brekken (1998) reported an annual average steady-state ·OH concentration of 2.1×10^{-18} M in a Southern California river.

Decide whether direct or indirect photolysis is dominant for photochemical transformation of NDMA in Southern California rivers. Conduct quantitative analysis to answer. Assume ·OH is the only relevant photochemically-produced reactive intermediate (PPRI) for indirect photolysis of NDMA.

(10 points)

Answer)

The direct photolysis rate,

$$k_p = k_a \times \Phi_r = 0.12 \sim 0.24\, einstein/mole-hr \times 0.41\, mole/einstein = 0.0492 \sim 0.0984/hr$$

The indirect photolysis rate,

$$k_{ip} = k_2 \times [\cdot OH]_{ss} = (4.0\times10^{8}\, L/mole-s)\times(2.1\times10^{-18} M) = 8.4\times10^{-10}/s = 3.02\times10^{-6}/\mathrm{min}$$

Because the direct photolysis rate is more than four orders of magnitude greater than the indirect photolysis rate, direct photolysis is dominant for NDMA transformation.

7. The pesticide DDT (MW = 354.5) has the following properties:

Vapor pressure = $10^{-9.87}$ atm (25℃)
Aqueous solubility = $10^{-7.85}$ mole/L (25℃)
Octanol-water partitioning coefficient, $K_{ow} = 10^{6.36}$

1) Calculate the Henry's constant at 25 ℃ expressed as a dimensionless concentration ratio, H_{cc}. (5 points)

Answer)

$$H_{PC} = \frac{P^{sat}}{C^{sat}} = \frac{10^{-9.87}\, atm}{10^{-7.85}\, mole/L} = 9.55\times10^{-3}\, atm-L/mole$$

$$H_{CC} = \frac{H_{PC}}{RT} = \frac{9.55 \times 10^{-3}\, atm - L/mole}{8.21 \times 10^{-2}\, L - atm/mole - K \cdot 298\, K} = 3.90 \times 10^{-4}$$

2) In a 40-mL vial, you added 5 g soil and 20 mL water, spiked some DDT, and agitated the contents until equilibrium was established. The air volume in the vial was 17 mL. Determine how mass of the spiked DDT is distributed at each phase (i.e., mass fraction in air, water, and soil relative to the total mass spiked). The soil-water distribution coefficient, K_d, is estimated to be 1.5×10^5 L/kg.

(14 points)

Answer)

$$Z^{air} = \frac{1}{RT} = 0.0409\, mole/L - atm$$

$$Z^{water} = \frac{1}{H_{PC}} = \frac{1}{9.55 \times 10^{-3}\, atm - L/mole} = 105\, mole/L - atm$$

$$Z^{soil*} = \frac{K_d}{H_{PC}} = \frac{1.5 \times 10^5\, L/kg}{9.55 \times 10^{-3}\, atm - L/mole} = 1.57 \times 10^7\, mole/kg - atm$$

$$\sum ZV = 0.0409\, mole/L - atm \cdot 0.017\, L + 105\, mole/L - atm \cdot 0.020\, L + 1.57 \times 10^7\, mole/kg - atm \cdot 0.005\, kg$$

$$= 7.85 \times 10^4\, mole/atm$$

Mass fraction in the air: $\frac{Z^{air} V^{air}}{\sum ZV} = \frac{0.0409\, mole/L - atm \cdot 0.017\, L}{7.85 \times 10^4\, mole/atm} = 8.86 \times 10^{-9}$

Mass fraction in water: $\frac{Z^{water} V^{water}}{\sum ZV} = \frac{105\, mole/L - atm \cdot 0.020\, L}{7.85 \times 10^4\, mole/atm} = 2.68 \times 10^{-5}$

Mass fraction in soil: $\frac{Z^{soil*} M^{soil}}{\sum ZV} = \frac{1.57 \times 10^7\, mole/kg - atm \cdot 0.005\, kg}{7.85 \times 10^4\, mole/atm} = 1.000$

3) Qualitatively predict the fate of DDT applied to agricultural area. Neglect the transformation reactions of DDT. (8 points)

Answer)

DDT will be highly sorbed to soil and remain in the surface soil, not substantially being transported vertically to be found in deeper soils. The compounds will neither be substantially volatilized to the atmosphere. While surface soils are flushed by surface runoff, DDT associated with them may follow the movement of the soil particles to be introduced into water bodies. When the soils settle down to the bed of river/stream/lake/ocean, DDT will settle down together, being present there for a long period of time unless any sediment resuspension occurs.