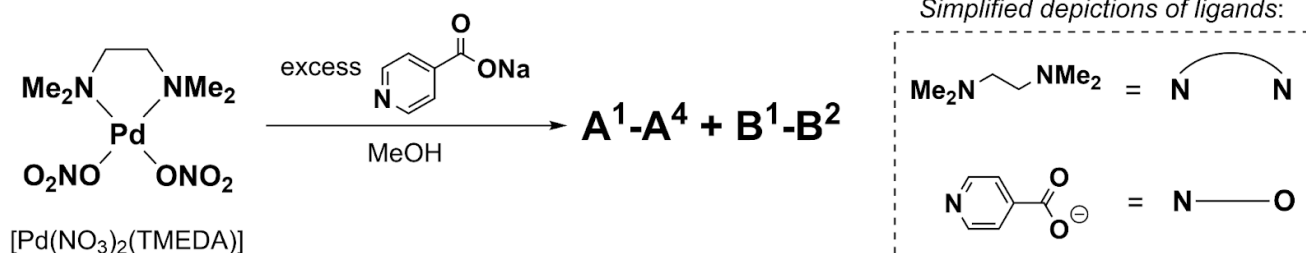


## Problem 1. Polygonal chemistry

The palladium complex  $[\text{Pd}(\text{NO}_3)_2(\text{TMEDA})]$  reacts with sodium isonicotinate (simplified as NaL) in a 1 : 1 ratio to yield a mixture of multinuclear complexes **A** and **B**, which resemble the simplest equilateral polygons by structure. The empirical formula of both complexes is  $[\text{PdL}(\text{TMEDA})]\text{NO}_3$ , where **A** can exist as four different isomers ( $\text{A}^1\text{-A}^4$ ) and **B** as two isomers ( $\text{B}^1\text{-B}^2$ ).



- Write the systematic name for the complex  $[\text{Pd}(\text{NO}_3)_2(\text{TMEDA})]$ .
- Sketch the structures of inner coordination spheres of complexes  $\text{A}^1\text{-A}^4$  and  $\text{B}^1\text{-B}^2$  using the provided structural simplifications to represent TMEDA and the isonicotinate anion ( $\text{L}^-$ ). Ignore overall charges and counterions in your structures.

Complexes **A** and **B** can interconvert in solution. Their chemical equilibrium is described by the equation  $a\text{A} \rightleftharpoons b\text{B}$ , where  $a$  and  $b$  are integer coefficients. The forward equilibrium constant has a value  $K_1 = 21.5$  at  $t_1 = 40.0$  °C and  $K_2 = 32.1$  at  $t_2 = 60.0$  °C. For the sake of simplicity, assume all isomers of **A** have the same Gibbs free energy of formation and all isomers of **B** also have the same Gibbs free energy of formation.

- Determine the smallest possible integer values for coefficients  $a$  and  $b$ .
- Calculate the value of the forward equilibrium constant  $K_3$  at  $t_3 = 50$  °C.
- Approximate the ratio  $[\text{B}] : [\text{A}]$  in solution at  $t_3 = 50$  °C if the analytical concentration of palladium in solution is  $c_0 = 1.154$  mM. Assume that in solution,  $\text{Pd}^{2+}$  exists only as part of complexes **A** and **B**.

## Problem 2. Unknown amino acid

0.3425 g of unknown amino acid **X** sample was treated with hot concentrated sulphuric acid, which converts organically bound nitrogen to ammonium salt. Then, an excess of concentrated sodium hydroxide solution was added to the previously obtained solution containing ammonium ions. Generated ammonia was distilled into 40.00 cm<sup>3</sup> of 0.1350 M hydrochloric acid. Finally, the excess of hydrochloric acid was titrated with 16.83 cm<sup>3</sup> of 0.1500 M sodium hydroxide solution. In the following calculations, assume that all produced ammonia reacts with hydrochloric acid.

- Calculate the mass percentage (%) of nitrogen in the sample.
- Calculate the pH value of the hydrochloric acid solution after the titration when 16.83 cm<sup>3</sup> of 0.1500 M sodium hydroxide solution has been added.  $\text{p}K_a(\text{NH}_4^+) = 9.25$ .

In nature, **X** occurs in its *L*-isomer form, which has two adjacent stereocenters. The dissociation constants of **X** are  $K_{a1} = 8.13 \cdot 10^{-3}$  and  $K_{a2} = 7.94 \cdot 10^{-10}$  (25 °C).

- Determine the condensed structural formula of **X**.
- Draw all the possible stereochemical structures for **X** using wedge-dash notation. Indicate the absolute configurations (*R/S*) of the stereocenters on all the structures.

- e) Select from the table above and draw the stereochemical structures of **X** *L*-isomer for the major ionic forms in aqueous solution at **(i)** pH 1.50, **(ii)** pH 6.00, and **(iii)** pH 11.00.
- f) Calculate the pH value of the aqueous **X** solution at its isoelectric point, where the overall charge of the ionic amino acid species is zero.

### Problem 3. Reverse engineering

A teacher is making a standard kinetics task for an exam, starting from desired answers that are easy to grade – 30 s and 60 kJ mol<sup>-1</sup>. Assist him in making the task! Consider a first-order kinetic reaction  $A \rightarrow B$  at  $T_1 = 300$  K. The initial concentration  $[A]_0$  is 1 M, and the concentration  $[A]_t$  after time  $t$  is 0.05 M.

- a) Calculate the reaction rate constant  $k$  value corresponding to  $t = 30$  s.
- b) Calculate the activation energy  $E_a$  value corresponding to  $t = 3$  s at  $T_2 = 2024$  K.

The calculated  $E_a$  value turns out to be too small. Which parameters (if changed individually) can the teacher adjust to make up a more reasonable activation energy?

- c) Select parameter(s) that affect activation energy  $E_a$ :  $T_1$ ,  $[A]_0$ ,  $[A]_t$ ,  $t$ .
- d) Recalculate the values of the selected parameters to give  $E_a = 60$  kJ mol<sup>-1</sup>.

The teacher continued reverse engineering by designing a four-step mechanism that gives a desired reaction law ( $-d[A]/dt = 2k_1k_2[A]/(k_{-1}+2k_2)$ ) assuming a steady state for  $A'$  and  $B'$ :



- e) Write the equations for the missing elementary steps. Show that your mechanism corresponds to the given reaction law.

### Problem 4. Have you heard about cerium?

#### Part I. Minerals

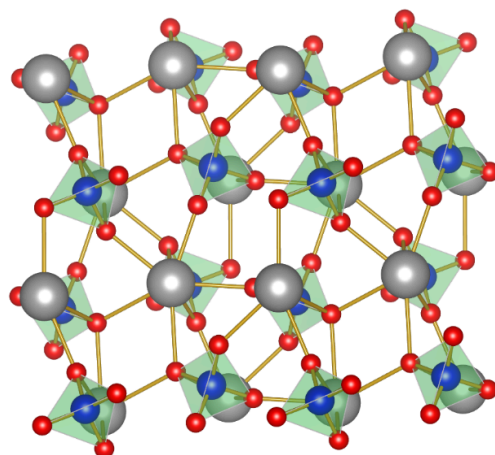
Monazite (Ce,La,Nd,Th)PO<sub>4</sub> and Bastnäsite (Ce,La)CO<sub>3</sub>F are the most common natural sources for cerium and other lanthanides such as lanthanum or neodymium. The monazite structure is made up of the arrangement of separate PO<sub>4</sub> tetrahedra, which are somewhat distorted but joined to one another by Ce (or other lanthanide) atoms. Monazite has a primitive monoclinic lattice system with  $\alpha = \gamma = 90^\circ$  and  $\beta = 103.63^\circ$ . The structure of this mineral is shown (colors of atoms: Ce – grey, P – blue, O – red).

- a) How many atoms are in the unit cell of monazite-(Ce)? *Hint: A unit cell is the smallest group of atoms from which the entire lattice can be built up by repetition in three dimensions.*
- b) Presence of which element makes the natural monazite radioactive: **i)** La, **ii)** Nd, **iii)** Th?

Part of the Ce atoms were artificially substituted by U atoms in the pure CePO<sub>4</sub> monazite crystal of 15.23 g. The mass of the resulting mineral was 19.76 g.

- c) Calculate the fraction of Ce atoms that were replaced.

U–Pb dating is one of the oldest and most refined of the radiometric dating schemes. The method relies on two separate decay chains, the uranium series from <sup>238</sup>U to <sup>206</sup>Pb, with



a half-life of 4.47 billion years, and the actinium series from  $^{235}\text{U}$  to  $^{207}\text{Pb}$ , with a half-life of 710 million years. Since the exact rate at which uranium decays into lead is known, the current ratio of lead to uranium in a sample of the mineral can be used to reliably determine its age if any lead found in the mineral is radiogenic. Consider a monazite rock (from Kollam, India) of 6.05 g which has 0.37%  $^{238}\text{U}_2\text{O}_3$  and 0.01% PbO by mass.

**d)** Calculate the approximate age of this mineral. Assume that only the uranium series decay chain occurs, and the presence of Pb is only due to the decay of radioactive  $^{238}\text{U}$ .

Bastnäsite usually occurs in a reddish brown color and can even be yellow depending on the ratio of metal ions present in the mineral. To identify the empirical formula of bastnäsite, the specimen with the formula of  $\text{Ce}_{0.48}\text{La}_x\text{Nd}_y\text{Pr}_{0.04}\text{Sm}_{0.01}\text{CO}_3\text{F}$  and weighing 3.1184 g was taken from Gallinas Mountains in New Mexico, USA. During mineral analysis, 0.6260 g of  $\text{CO}_2$  after acidic treatment with diluted  $\text{H}_2\text{SO}_4$  was captured.

**e)** Find an empirical formula for this mineral sample if all metal atoms have an oxidation number +3.

The crystal structure of bastnäsite is quite complex. Yet, one can simplify it to hexagonal closest-packed (HCP) unit cell. In the Figure, Ce atoms are orange, and all other atoms (whether they are C, O, or F) are black.

**f)** What is the coordination number of Ce in this structure?

Among lanthanides, cerium is the easiest to extract from its minerals because it is the only one that can reach a stable +4 oxidation number in aqueous solutions. While roasting the bastnäsite, most of the lanthanides are oxidized to  $\text{Ln}_2\text{O}_3$ , except cerium which forms the water-insoluble dioxide  $\text{CeO}_2$ .

**g)** Calculate the volume  $\text{m}^3$  of 0.50 M HCl needed to leach  $\text{CeO}_2$  after roasting  $5.00 \cdot 10^3$  kg of bastnäsite with 32% Ce by mass. Write the equation of this extraction reaction in the tank.

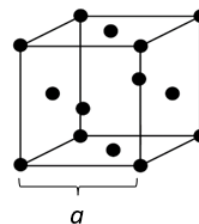
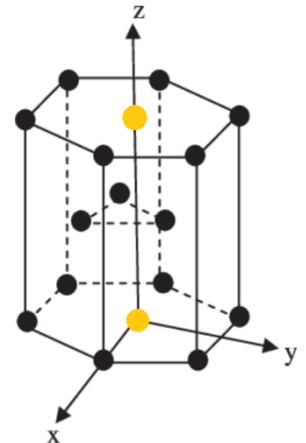
Four allotropic forms of cerium exist at standard pressure. The stable form below 726 °C to approximately room temperature is  $\gamma$ -cerium, with a face-centered cubic (FCC) crystal structure. The double hexagonal close-packed form (DHCP), known as  $\beta$ -cerium, is the equilibrium structure approximately from room temperature to -150 °C. Upon cooling below -15 °C,  $\gamma$ -cerium starts to change to  $\beta$ -cerium, but the transformation proceeds slowly.

**h)** Calculate and compare the density of  $\beta$ -cerium ( $a = 0.3681$  nm,  $c = 1.1857$  nm) and  $\gamma$ -cerium ( $a = 0.5161$  nm) in  $\text{g cm}^{-3}$ .

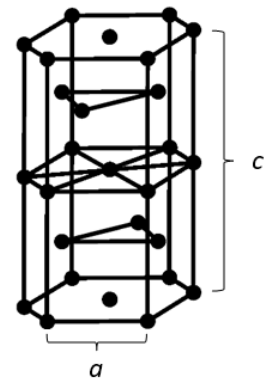
## Part II. Cerium loves redox

Cerium extracted from the ores is used to produce certain laboratory reagents such as ceric ammonium nitrate (abbreviated as CAN)  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ . CAN is often used in redox reactions for quantitative analysis, especially iron determination. Consider the reaction of CAN with the soil sample.

**i)** Write the ionic equation of this one-electron oxidizing reagent reacting with the mixture of green rust  $\text{Fe}(\text{OH})_2$  and 4 times smaller amounts of cuprite  $\text{Cu}_2\text{O}$  in acidic conditions.



FCC unit cell



DHCP unit cell

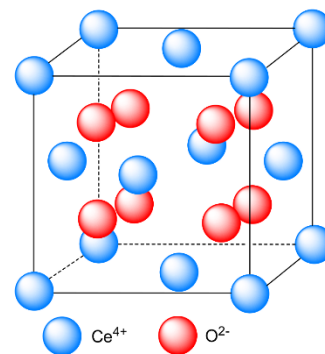
j) Draw the structure of the anion of CAN if the central atom and its neighbors form an icosahedron.

A is a pale white powder and contains 25.11% O by mass. By modifying the oxidation number of oxygen atoms in A, a reddish-brown color substance B is formed. B contains oxygens that differ in their oxidation numbers. B is converted to C by heating the solution and can be prepared using strong oxidizers like PbO<sub>2</sub>. All oxygen atoms in C have the same oxidation number.

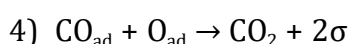
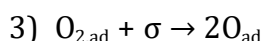
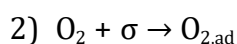
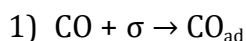
k) Identify A–C and write the equations: i)  $\text{Ce} + \text{H}_2\text{O} \rightarrow \text{A} + \text{H}_2$ ,  
 ii)  $\text{A} + \text{HO}_2^- \rightarrow \text{B} + \text{H}_2\text{O} + \text{OH}^-$ , iii)  $\text{B} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{C} + \text{HO}_2^-$ .

l) Fill in the gaps in the text and choose correct answers.

Ceria (CeO<sub>2</sub>) plays a special role in heterogeneous catalysis. In the ideal lattice of CeO<sub>2</sub>, the structure consists of a **primitive cubic** / **body-centered cubic** / **face-centered cubic** unit cells of cations with anions occupying the **cubical** / **tetrahedral** / **octahedral** holes. In the structure, each cerium cation is coordinated by \_\_\_ nearest-neighbor oxygen anions, while each oxygen anion is coordinated by \_\_\_ nearest-neighbor cerium cations. Ceria can also be doped with other metal cations to alter electric conductivity. When cerium cations are replaced with lower oxidation number elements (M<sup>2+</sup>/M<sup>3+</sup>), the lattice oxygen atoms in CeO<sub>2</sub> are **incorporated** / **removed**. The ceria crystal usually exhibits a few defects due to the co-existence of Ce<sup>4+</sup> and \_\_\_\_\_ ions.



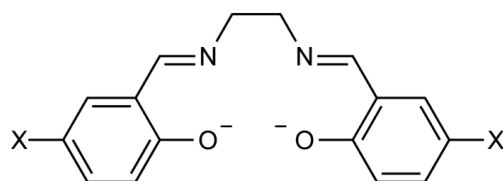
One of the applications of CeO<sub>2</sub> resides in automotive catalysis and offers a more efficient way to convert CO to CO<sub>2</sub>. The challenging part here is that the oxidation of CO and hydrocarbons must be carried out simultaneously with the reduction of pollutant I. The harsh conditions experienced in the catalytic converter dictate that the catalysts be based on precious metals (e.g., Pt, Rh, and Pd), but precious metals are not selective for oxidizing CO and hydrocarbons using I in the presence of J. However, an altered catalyst is made by vapor depositing catalytic metals onto polycrystalline ceria films to improve the situation. When excess J is present in the exhaust stream, it is removed by adsorption onto reduced ceria so that CO and hydrocarbons are oxidized by reducing J. When there are insufficient amounts of I and J in the exhaust to oxidize the CO and hydrocarbons, ceria releases K. K transfer from ceria to precious metal is important for catalysis. In excess CO, the kinetics for this reaction over bulk Pt, Pd, and Rh are very well understood and are described by Reactions 1-4 (written in the end), where σ represents an empty site on the metal. Because the metal surfaces are essentially saturated in CO when excess CO is present, the rate-limiting step for the reaction is \_\_\_. With ceria-supported metals, there is an additional pathway 5 for forming O<sub>ad</sub> by the transfer of oxygen from ceria to the metal that speeds up the overall conversion. Because ceria does not adsorb CO, the reoxidation of L, reaction 6, is not affected by the coverage of CO on the metal. Using steam as the oxidant, 6 is replaced by 7 which is a very important reaction for the production of M.



m) Identify formulas of compounds and elements I, J, K, L, and M.

n) Write equations of reactions 5, 6, and 7.

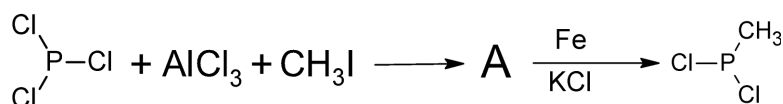
Ce (IV) forms 8-coordinate bis(salen) complexes. A 5,5'-X<sub>2</sub>-salen ligand is shown.



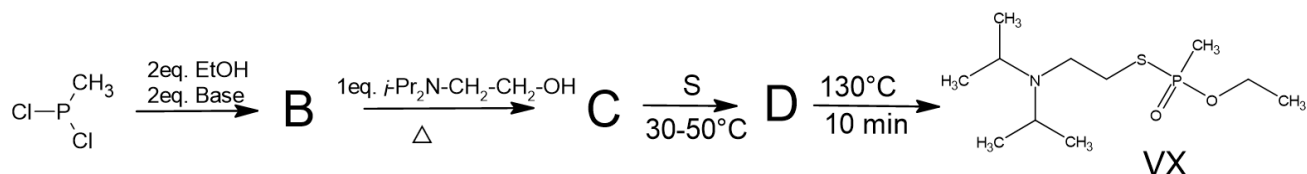
- o) Which complex – Ce(5,5'-(OMe)<sub>2</sub>-salen)<sub>2</sub> or Ce(5,5'-(Cl)<sub>2</sub>-salen)<sub>2</sub> – is a stronger oxidizing agent?

## Problem 5. Poisonous chemicals

S-[2-(diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (**VX**) is an odorless, colorless, human-made chemical developed in 1952. It is the most toxic, rapidly acting of all compounds classified as nerve agents. Not found naturally in the environment, **VX**'s only application is in chemical warfare. It is classified as a weapon of mass destruction by the United Nations in UN Resolution 687, and the production and stockpiling of **VX** was outlawed by the Chemical Weapons Convention of 1993. The synthesis of VXs starts with a two-step reaction of phosphorus trichloride with methyl iodide.



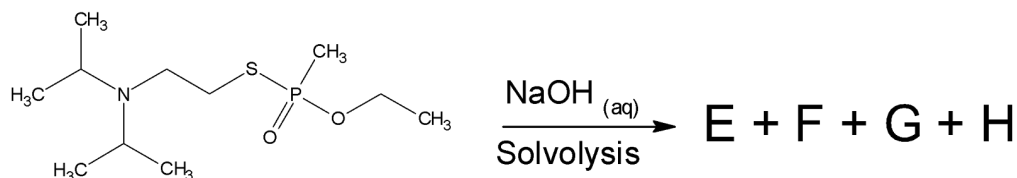
- a) Draw the structural formula of intermediate **A**.  
 b) Draw the structural formulas of compounds **B–D**.



Affected by high temperature product **D** starts isomerisation to **VX**.

- c) Draw the isomerization mechanism from product **D** to **VX**.  
**VX** is produced *via* the thermal process, which gives a racemic mixture of enantiomers.  
 d) Mark chiral centers in **VX** molecule.  
 e) How many possible stereoisomers does **VX** have?

Like other organophosphorus nerve agents, **VX** may be destroyed by a reaction with strong nucleophiles. The reaction of **VX** with concentrated aqueous sodium hydroxide results in two competing solvolysis reactions, giving four different compounds (**E–H**).



- f) Write structural formulas of compounds **E–H**.  
 g) Which one of the **E–H** compounds is still highly toxic?

Despite solvolysis, it was found that **VX** can go the third way of degradation. The third degradation pathway becomes dominant under certain conditions. It involves the C-S bond cleavage to form products **I** and **J**.



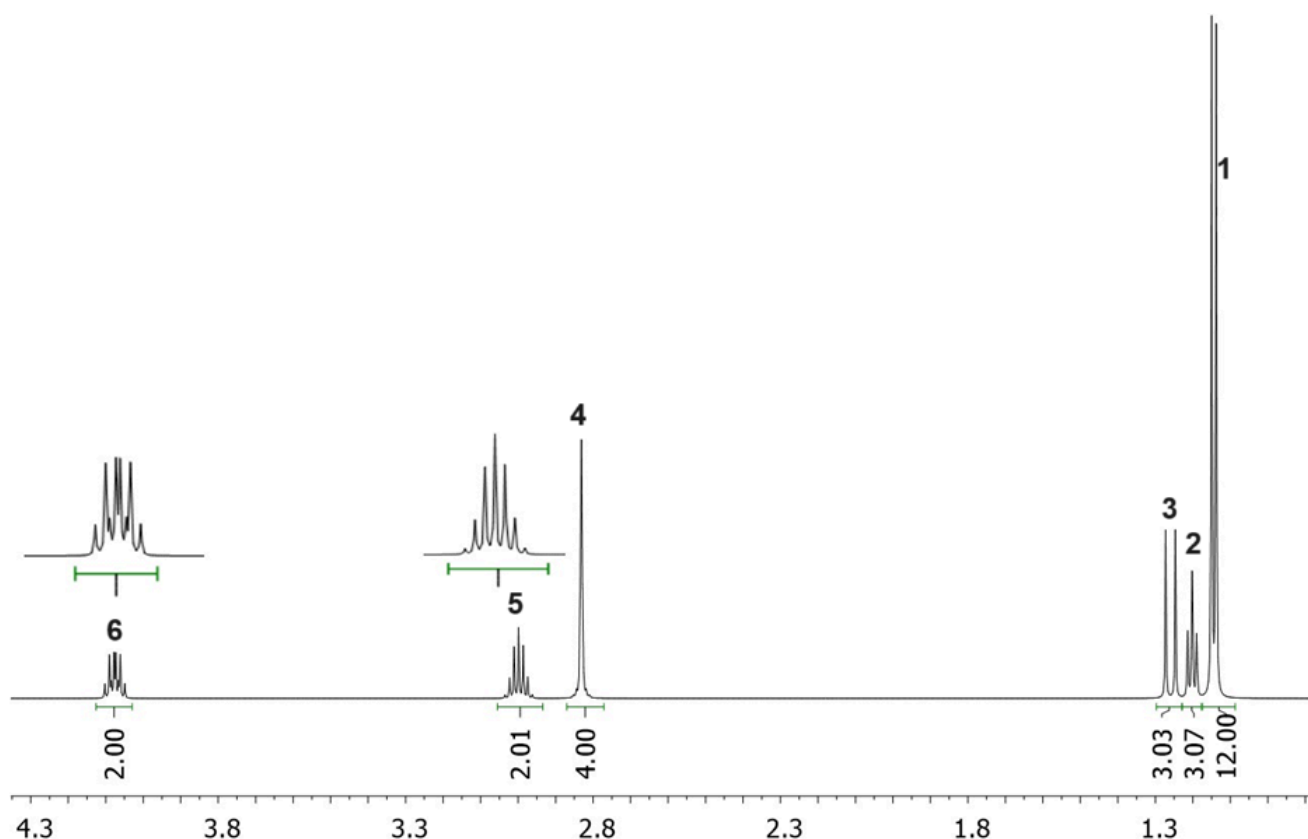
**h)** Draw the structural formulas of compounds **I** and **J**.

The  $^1\text{H}$  NMR spectrum of the **VX** (in  $\text{CDCl}_3$ ) is given below.

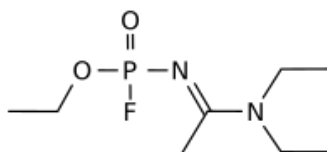
**i)** Assign the corresponding  $^1\text{H}$  NMR signals for **VX**.

**j)** Indicate chemical element(s) that cause peak splitting in compound **VX**  $^1\text{H}$  NMR spectrum.

**k)** Assign the multiplicity of peaks (**1-6**) in the  $^1\text{H}$  NMR spectrum.



The agent A-234 is supposedly around five to eight times more potent than **VX**.



The median inhaled A-234 lethal dose for an 80 kg person has been estimated as  $7 \text{ mg m}^{-3}$  for two-minute exposure when the person inhales  $15 \text{ dm}^3$  per minute.

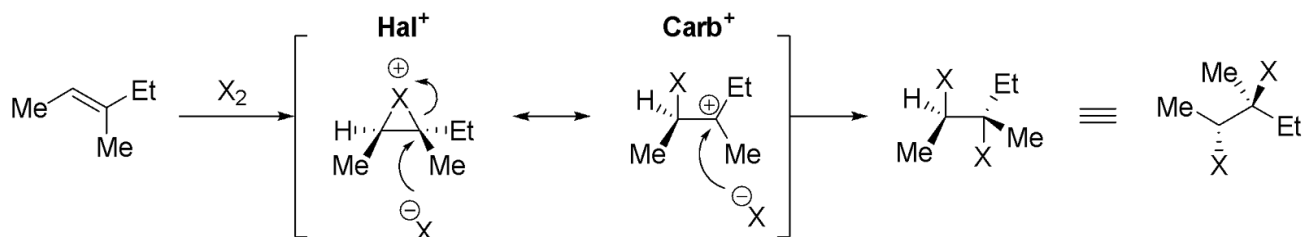
**l)** Calculate the lethal dose of agent A-234 in grams.

**m)** Calculate the lethal dose in grams per kilogram of a person's weight.

**n)** How many lethal doses are in 1 gram of this compound for a 100 kg person?

## Problem 6. Simple organic chemistry

Alkenes react with halogens through a three-membered cationic halonium ion intermediate **Hal<sup>+</sup>**, which is in resonance with a carbocation **Carb<sup>+</sup>**. Both resonance forms explain selectivity in this reaction: halonium **Hal<sup>+</sup>** dictates that the addition of X<sub>2</sub> is anti (on opposite sides), and carbocation **Carb<sup>+</sup>** dictates that attack of halide anion (or a different nucleophile) takes place at the most substituted carbon atom.



Let us look at monoalkenes with a molecular formula of C<sub>5</sub>H<sub>8</sub>. Assume that all these isomers are stable and obtainable.

- a) Determine the number of **i)** 5-membered ring, **ii)** 4-membered ring, and **iii)** 3-membered ring isomers, considering stereochemistry.

A symmetrical isomer of this group reacted with Br<sub>2</sub> in a nonpolar solvent and formed only one stereoisomer.

- b) Draw the structural formula of this isomer.  
c) What would be the product of bromination in methanol?

A monoalkene **H1** with a molecular formula C<sub>4</sub>H<sub>6</sub> reacted with bromine and produced three structural isomers **B1–B3**. The <sup>1</sup>H NMR data of **B1–B3** (in CDCl<sub>3</sub>) are given below.

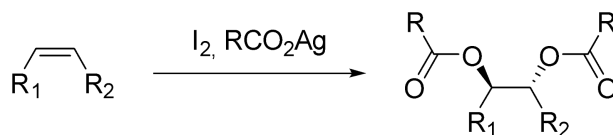
**B1:** <sup>1</sup>H NMR 4.02 (s, 2H), 1.38–1.32 (m, 2H), 1.10–1.03 (m, 2H)

**B2:** <sup>1</sup>H NMR 5.67 (s, 2H), 4.31 (s, 4H)

**B3:** <sup>1</sup>H NMR 3.24 (m, 4H), 2.20 (m, 2H)

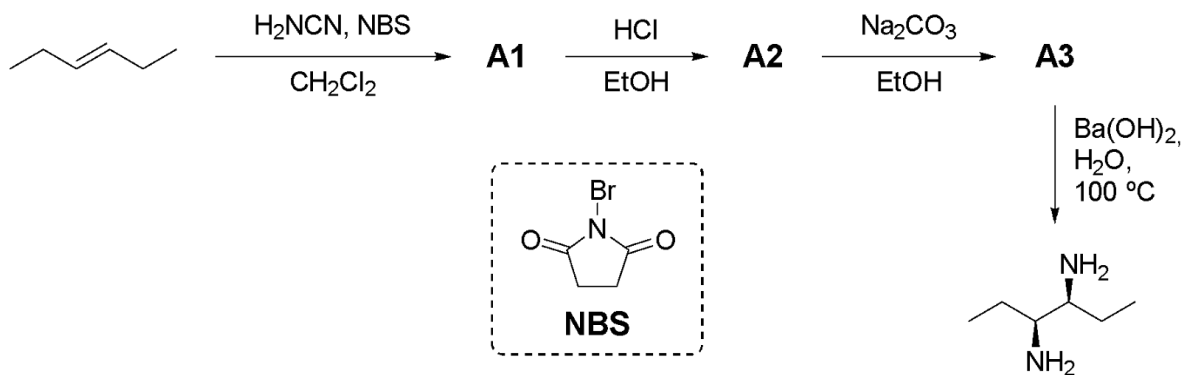
- d) Draw the structural formulas of compounds **H1** and **B1–B3**.

The formation of halonium ion is typically used as an intermediate in more complex transformations. For example, the Prevost reaction allows to obtain diesters in an anti-fashion:



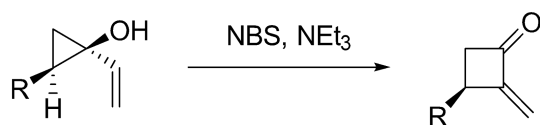
- e) How many stereoisomers are formed in this reaction if **i)** (R<sub>1</sub> = R<sub>2</sub>) ≠ H and **ii)** (R<sub>1</sub> ≠ R<sub>2</sub>) ≠ H? Since the product (diester) has 2 chiral carbon atoms, how many stereoisomers exist in total if **i)** (R<sub>1</sub> = R<sub>2</sub>) ≠ H and **ii)** (R<sub>1</sub> ≠ R<sub>2</sub>) ≠ H?  
f) Draw the mechanism of the Prevost reaction. Note that the relative configuration of the product is anti.

Halonium ion can also be used as an intermediate in the synthesis of 1,2-diamines:



**g)** Draw the structural formulas of compounds **A1–A3**, including stereochemistry.

Halonium ion is also an intermediate in some rearrangements, such as semipinacol rearrangement, which leads to a ring expansion:



**h)** Draw the reaction mechanism.