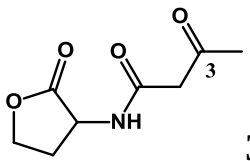
CHEMISTRY 1 – Test n°3 – Duration : 3 hours

No document allowed. Only « collège » type calculators are authorized.
Each answer must be justified. Caution: marking is for information only: 40 points
Useful data are provided at the end of the subject (page 4)



3-oxo-butanoyl homoserine lactone

The N-acyl homoserine lactones (see an example above) are used by bacteria to communicate with each other. Indeed, they allow bacteria for synchronizing their biological activities and the expression of genes as a function of their density of population (a phenomenon called "quorum sensing").
The **3-oxo-butanoyl homoserine lactone** has been studied by X-ray diffraction at a temperature of 100 K. **Exercise I-A** deals with the production of X-rays, then their absorption by a metal **M**. The crystalline structure of **zirconium** is the topic of **exercise I.B** as nanoparticles made of zirconium oxide ZrO_2 have been studied by researchers for their antibacterial activity**.** Then the crystalline structure for 3-oxo-butanoyl homoserine lactone is the topic of **exercise I.C. Exercise II** deals with the molecular structure and one (small) part of the chemical reactivity of the homoserine lactone. Finally, the emission spectrum of a hydrogen-like ion is studied in **exercise III**.

Each exercise can be solved independently.

EXERCISE I : X-Rays and crystalline structures (20.5 pts)

I.A - Production of X-rays

|E| in eV for elements Fe, Zn, and the unknown metal M

Levels	K	L_1	L_2	L_3	M_1	$M_{2,3}$	$M_{4,5}$
Fe	7112.0	846.10	721.10	708.10	92.900	54.000	3.6000
Zn	9658.6	1193.6	1042.8	1019.7	135.90	86.600	8.1000
M	8978.9						

The X-rays beam is produced by a device exposed to a difference of potential equal to 12kV using an anticathode made of **zinc**. In the range of wavelength of interest (lower than 2 Å), the resulting spectrum is mainly made of 3 rays which characteristics wavelength and respective intensity are gathered in the following table:

# Ray	1	2	3
λ (Å)	1.2954	1.4353	1.4392
I	0.25 I_0	I_0	0.5 I_0
μ (cm^{-1}) for a screen made of metal **M**	2319.2	356.8	374.6

1) What is the threshold value of the continuous background (to within 10^{-4} Å)? How does this value vary with the atomic number Z of the anticathode when the same difference of potential is applied?
2) Give the specific transition associated to each of the ray given in table available on page 1. Justify your answers.
3) **Using the data and computations above,** schematize the resulting X-rays spectrum with all the numeral values that are known.
4) What is the atomic number of metal **M**?
5) Give the electronic structure for metal **M**. To which period, group and block of the periodic table does it belong to?
6) Can the K-L_3 ray of zinc promote the X fluorescence of iron or the one of metal **M**, respectively? Justify your answers.
7) When crossed by the X-ray beam obtained with the anticathode made of zinc: would metal **M** be an efficient filter to result in a beam mainly composed of rays N°2 and 3? Justify your answer.
8) Determine the thickness x (in µm) of the filter made of metal **M** such that 99.0% of the incident intensity of ray N°1 is absorbed.
9) What would be the ratio (I_2/I_3) of the intensity of the rays obtained after passing the filter for the λ_2 and λ_3 wavelengths, if a filter with a thickness of 25.0 µm was used?

I.B – Study of the crystalline structure for zirconium

Zirconium crystallizes in a hexagonal close-packed structure (atoms are tangent along the edges of the base, with a supplementary atom located such that its reduced coordinates are (2/3,1/3,1/2) in the direct system of vectors associated to this cell). Moreover, the *c* cell parameter is such that c = 5.148 Å.

1) Give the electronic structure of zirconium and the most encountered oxidation degrees.
2) Give the Bravais lattice (crystalline system + centering) and the composition of the motif for zirconium.
3) Calculate the *a* cell parameter for the hexagonal cell (to within 10^{-3} Å). It is recalled that c/a = $2\sqrt{2/3}$ for such crystalline structure.
4) On a simple hexagonal cell, identify clearly the (001) and (100) planes, respectively.
   Are {001} and {100} families of reticular planes?
   If yes, then give the inter-reticular distance for each respective family (to within 10^{-3} Å).
5) Calculate the radius for an atom of zirconium, in Å (to within 10^{-3} Å).

I.C – Study of the crystal structure of the 3-oxo-butanoyl homoserine lactone

The 3-oxo-butanoyl homoserine lactone of crude formula $C_8H_{11}NO_4$ crystallizes in a structure with parameters $\alpha = \beta = \gamma = 90°$. This compound was studied by X-rays diffraction. The obtained diffractogram shows the following peaks:

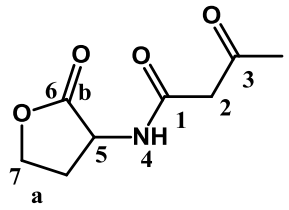
d (Å)	4.4770	5.9223	4.3413	2.4860	3.2036	2.2209	2.2173
h, k , l	1 1 0	0 0 3	1 1 1	2 0 1	2 2 1	3 1 1	1 4 0

1) Compute to within 10^{-3} Å the a, b and c parameters of the cell.
2) Deduce the crystalline system.
3) Knowing that a cell contains 4 molecules, compute the density ρ ($g.cm^{-3}$)
4) Give the possible Bravais lattices for this crystalline system.
   Give the extinction conditions on (h, k, l) that apply to every cited Bravais lattice.
   Deduce the Bravais latice of 3-oxo-butanoyl homoserine lactone.
5) Give the symmetry axes observed in this system.

6) On two different schemes representing the cell, draw the first plane of the families of Miller indices {111} and {201}.

Problem II Structure and reactivity of the 3-oxo-butanoyl homoserine lactone (13.5 pts)

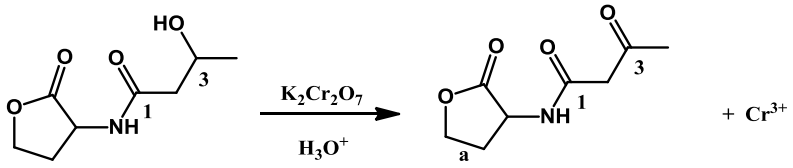
II.A Structure of the 3-oxo-butanoyl homoserine lactone.



1) Draw the structure of the 3-oxo-butanoyl homoserine lactone adding the non-bonding doublets.
2) Is it possible to draw mesomeric formula(s) of this molecule involving the Nitrogen atom? If yes, which ones?
3) Give the hybridization states of the 6 atoms numbered from 1 to 6.
4) What are the approximate values of the angles observed around atoms 1 and 7, respectively?
5) In the 3-oxo-butanoyl homoserine lactone, indicate the type of bonding for bonds a and b indicated on the scheme. Which atomic orbitals are involved in those bonds?

II.B Reactivity of homoserine lactones

The 3-oxo-butanoyl homoserine lactone is obtained by oxidation of 3-hydroxy-butanoyl homoserine lactone using potassium dichromate ($K_2Cr_2O_7$) in acidic media.



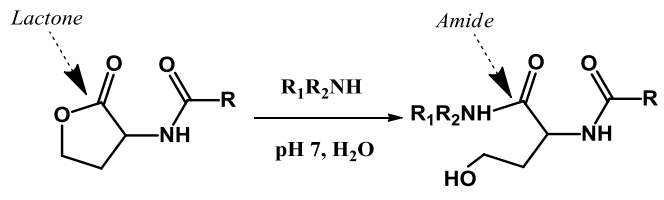
3-hydroxy-butanoyl homoserine lactone

3-oxo-butanoyl homoserine lactone

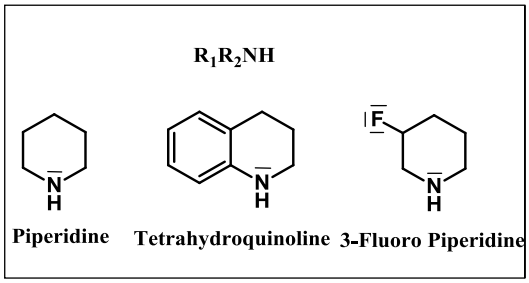
(To be balanced)

1) Give the Lewis structures of the dichromate ion ($Cr_2O_7^{2-}$; containing a Cr-O-Cr motif), of the hydronium ions (H_3O^+). Give the oxidation numbers of the Cr and O atoms in these structures. If existing, draw mesomeric formulas. Give the geometry and angle value around Cr for $Cr_2O_7^{2-}$ and O for H_3O^+, respectively.
2) a) Indicate the oxidized and reduced forms of the redox couples involved in the above global oxido-reduction reaction (qualify your answer).
   b) Write down the half-equations and give the balanced global reaction in acidic medium.
3) **Acido-basicity and nucleophilicity**

The reaction of a series of *N*-Acyl homoserine lactones with secondary amines of formulas R_1R_2NH in physiological conditions (pH = 7.0) have been tested. The availability of the non-bonding doublet (nucleophilicity) of the nitrogen atom in R_1R_2NH is responsible of the ring opening reaction. This transforms the lactone function into an amide function. (see scheme below).



N-Acyl homoserine lactone



a) Identify the acid-base couples belonging to the piperidine base family (in the box on the scheme above) and rank them by order of increasing pKa (qualify your answer).

b) Piperidine is the conjugated base of an acid-base couple with a pKa of 11.2. Deduce why the above reaction did not happen using piperidine.

Problem III Study of an hydrogen like ion spectrum (6 pts)

In this problem, to be considered good, every computation should be made on a clearly demonstrated and qualified literal expression.

1) A hydrogen like ion possess an ionization energy of 217.60 eV. Which hydrogen like ion is it? Identify it using the writing formula $_ZX^{n+}$.
2) Give the six first energy levels (computed to within 10^{-2} eV) of this hydrogen like ion.
3) What will happen if a sample of this hydrogen like ion is placed in an electromagnetic radiation of frequencies ranging between 5.0 10^{16} and 5.1 10^{16} Hz?
4) How many rays are found in the emission spectrum?
5) Among these rays, which electronic transition corresponds to a monochromatic radiation of wavelength 252.4 nm? To which domain of the electromagnetic spectrum does this radiation belong to?
6) Draw clearly on a Grotian's diagram of this hydrogen like ion including the characteristic levels and transitions considered above.

DATA

Rydberg's constant for Hydrogen: R_H = 109 677 cm^{-1} = R_X for hydrogen like ions.

Planck's constant: $h = 6.626\times10^{-34}$ J.s

Light speed: $c = 2.998 \times 10^{8}$ $m.s^{-1}$

Avogadro's constant $N_A = 6.022 \times 10^{23}$ mol^{-1}

Elementary charge: $e = 1.602 \times 10^{-19}$ C

Vacuum permittivity: $\varepsilon_0 = 8.854\times10^{-12}$ $F.m^{-1}$

Electron's mass: $m = 9.10939\times10^{-31}$ kg

Element	H	Li	Be	C	N	O	K	Cr	Fe	Ni	Cu	Zn	Ga	Zr
Z	1	3	4	6	7	8	19	24	26	28	29	30	31	40
M ($g.mol^{-1}$)	1	6	8	12	14	16	39	52	56	59	63.5	65.4	69.7	90.0
χ	2.1	1.0	1.5	2.5	3.0	3.5	0.8	1.6	1.8	1.8	1.9	1.6	1.6	1.4

χ is the electronegativity according to Pauli's scale

FORM

Beer-Lambert law: $I = I_0 \exp(-\mu x)$

Moseley's law: $\sqrt{\nu} = a(Z-b)$

Interplanar spacing :

$$\frac{1}{d_{hkl}^2} = \frac{\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma + \frac{2hk}{ab}(\cos\alpha\cdot\cos\beta - \cos\gamma)}{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cdot\cos\beta\cdot\cos\gamma}$$

$$+\frac{\frac{2kl}{bc}(\cos\beta\cdot\cos\gamma-\cos\alpha)+\frac{2lh}{ca}(\cos\gamma\cdot\cos\alpha-\cos\beta)}{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cdot\cos\beta\cdot\cos\gamma}$$

Relation between E and λ : E(eV) = 12400/λ(Å)