SChL

Singapore Chemistry League 2023

Atomic Rush Problems and Solutions

Problem Setters

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AR1: Up and up

A one-step endothermic reaction has an activation energy of +33.5 kJ mol^{-1} and a ΔH of +10.2 kJ mol^{-1}. Determine the activation energy of its reverse reaction in kJ mol^{-1}, at the same temperature.

Leave your answer in 3 significant figures. You may omit the + sign.

Solution:

23.3 kJmol^{-1}

The activation energy of the reverse reaction is the difference between the activation energy and the ΔH of the forward reaction. This relationship can be seen by drawing an energy profile diagram.
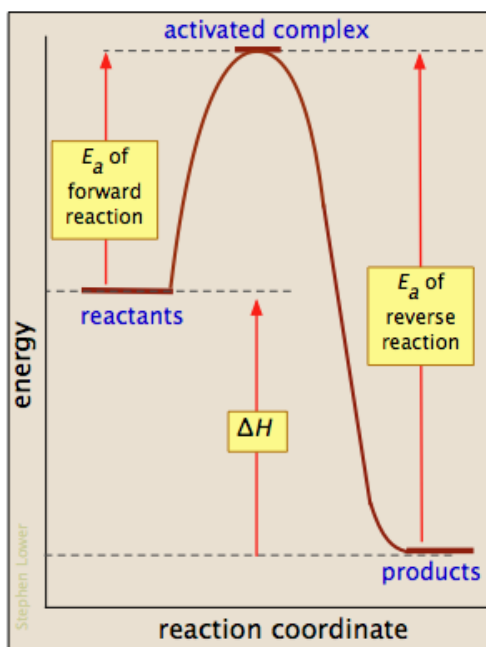
(Reference: Lower, S. (2018). "Collision and Activation: The Arrhenius Law." *Activation Energy, Arrhenius Law,* Simon Fraser University, 20 Mar. 2018, www.chem1.com/acad/webtext/dynamics/dynamics-3.html.)

Given the forward reaction is endothermic, the reverse reaction will be exothermic. The magnitude of ΔH remains the same. Hence the reverse reaction has $\Delta H = -10.2$ kJmol^{-1}.

$\Rightarrow E_a$ of reverse reaction $= 33.5 - 10.2 = 23.3$ kJmol^{-1}

AR2: Interhalogens

Interhalogens of the general form XY_n are commonly formed, where n = 1, 3, 5, 7. Anionic and cationic variants also exist, such as $[ClF_4]^-$.

How many valence lone pairs does IF_7 (shown below) have?
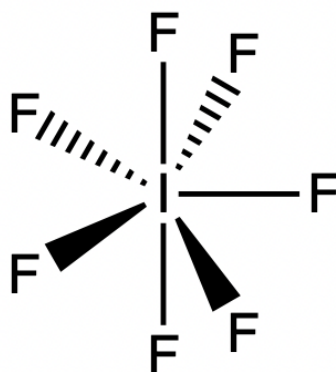
Solution:

21

There are no lone pairs on iodine and 3 lone pairs on each F atom, for a total of 21 lone pairs.

AR3: Chemistry practical flashbacks

It is given that it takes 8.01g of a hydrated $Mg(NO_3)_2 \cdot nH_2O$ to prepare 250cm^3 of 0.250 mol dm^{-3} nitrate ions. What is the value of n?

Solution:

6

In 250dm^3, there is $0.250(0.250) = 0.0625$ mol of NO_3^- ions. As the molar ratio of $Mg(NO_3)_2$ • nH_2O : NO_3^- produced is 1 : 2, this means 0.03125 mol of $Mg(NO_3)_2$ • nH_2O was used.

Thus $\dfrac{8.01}{Mr\ (Mg(NO3)2 \bullet nH2O)} = 0.03125$. This gives $M_r(Mg(NO_3)_2$ • $nH_2O) = 256.32$ (5s.f.), which corresponds to n = 6.

AR4: Making helium like there's no tomorrow

Nihonium-236[1] undergoes 6 successive alpha decays, the equation for which is given below. What is the sum of the mass number and proton number of the resulting nucleus?

$$^{A}_{Z}X \rightarrow\ ^{A-4}_{Z-2}X +\ ^{4}_{2}He$$

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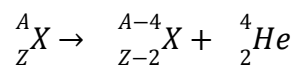
[1] The isotope Nihonium-236 does not exist in reality, but thanks to the sheer determination of the problem setter, it now does (in this question).

Solution:

313

Each alpha decay leads to the emission of one helium nucleus, $^{4}_{2}He$. In other words, each decay causes the mass number of the starting particle to decrease by 4, and the proton number to decrease by 2.

Mass number: $236 - 4 \times 6 = 212$
Proton number: $113 - 2 \times 6 = 101$
$212 + 101 = 313$. The resulting isotope is Mendelevium-212.

AR5: A Little Pressure

Container A contains 1 mol of gas X at pressure $2p$. An identical container B contains 2 mol of gas Y at pressure $3p$. What is the ratio of the temperature in container A to the temperature in container B?

Leave your answer in 3 significant figures.

Solution:

1.33

From the ideal gas equation pV = nRT, $R = \dfrac{p_x V_x}{n_x T_x} = \dfrac{p_y V_y}{n_y T_y}$.

Since V_x and V_y are identical, the above equation simplifies to $\dfrac{p_x}{n_x T_x} = \dfrac{p_y}{n_y T_y}$.

Rearranging, we have $\dfrac{T_x}{T_y} = \dfrac{n_y p_x}{n_x p_y}$.

Given $\dfrac{n_y}{n_x} = \dfrac{2}{1} = 2$ and $\dfrac{p_x}{p_y} = \dfrac{2p}{3p} = \dfrac{2}{3}$,

We get $\dfrac{T_x}{T_y} = \dfrac{4}{3} = 1.33$ (3 s.f.)

AR6: Purple trouble

0.00229 moles of $KMnO_4$ oxidises 0.00381 moles of $\mathbf{A}^{x+}$ to $\mathbf{A}O_3^-$ in an acidic medium, where $\mathbf{A}$ is an unknown element. Find the value of x.

Solution:

2

In AO_3^-, **A** has an oxidation state of $+5$.

5 mol of electrons are exchanged for every mol of $KMnO_4$ reduced to Mn^{2+} in acidic medium.
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
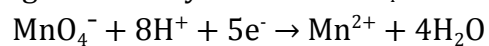
Molar ratio of $A^{x+} : KMnO_4 = 0.00381 : 0.00229 \approx 5 : 3$
If 3 mol of $KMnO_4$ is reduced, the reaction involves 15 mol of electron transfer.
Given 15 mol of electrons oxidises 5 mol of A^{x+}, one mol of A^{x+} will be oxidised by 3 mol of electrons, leading to an increase in oxidation state by 3.

Oxidation state of **A** in $A^{x+} = 5 - 3 = +2$
$\Rightarrow x = 2$

AR7: Rates

The rate of the gas phase isomerisation of **A** (g) ⇌ **B** (g) was investigated. The rate-time graph was shown below. The dashed line shows the rate of the forward reaction, and the solid line the rate of the reverse reaction.
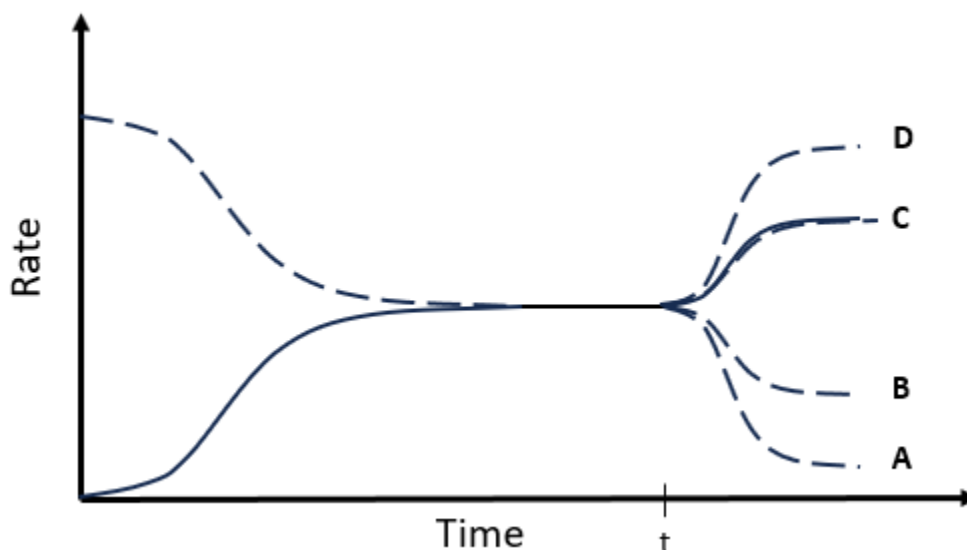
At time *t*, each of the following changes were made, and the rate of the reverse reaction is shown by the solid line.

1) A catalyst to produce **A** at a faster rate was added.
2) A catalyst to produce **B** at a faster rate was added.

Which of the dotted curves show how the rate of the forward reaction changes?

Present your answer as a single string comprising the answer to each part, in order. If your answer to part 1 is E, and your part to part 2 is F, leave your answer as EF.

Leave your answer as a string of two letters.
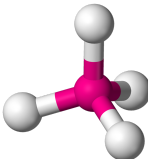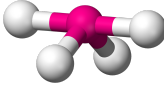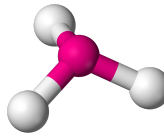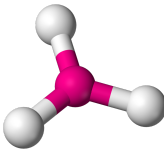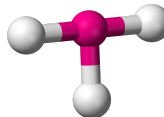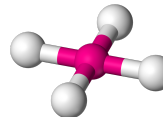
Solution:

CC

Catalysts increase the rate of the forward and reverse reactions by the same amount, and do not shift the position of equilibrium. Thus, from time t, the rate of the forward reaction should remain identical to the rate of the reverse reaction, and vice versa.

AR8: Ves-per, or V-S-E-P-R?

Match the following list of 4-atom and 5-atom molecules to its respective molecular shape, as predicted by VSEPR theory.

$[SO_3]^{2-}$	$[XeF_3]^+$	NO_2Cl	$ClOF_3$	$[ICl_4]^-$	NSF_3
a	**b**	**c**	**d**	**e**	**f**
Tetrahedral	Seesaw	Trigonal pyramidal	Trigonal planar	T-shaped	Square planar
1	**2**	**3**	**4**	**5**	**6**
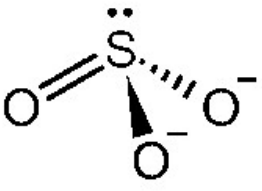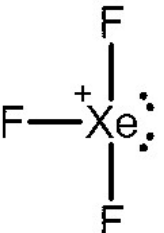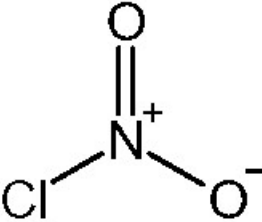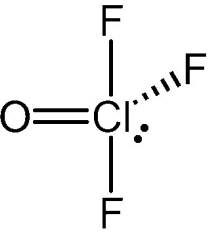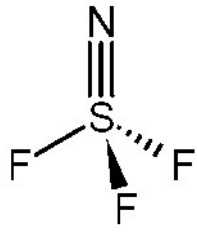
Type the corresponding numbers of each molecular shape in order as a string of numbers. For example, if you believe that molecule **a** has molecular shape **1**, **b** corresponds to **2**, **c** corresponds to **3** and so on, enter your answer as "123456".

Leave your answer as a 6-digit number.

Solution:

354261

Drawing out the Lewis structures, the geometries of the molecules are as follows:

$[SO_3]^{2-}$	$[XeF_3]^+$	NO_2Cl
No. of substituents = 3 No. of lone pairs on S = 1 Shape: **Trigonal pyramidal** (3)	No. of substituents = 3 No. of lone pairs on Xe = 2 Shape: **T-shaped** (5)	No. of substituents = 3 No. of lone pairs on N = 0 Shape: **Trigonal planar** (4)
$ClOF_3$	$[ICl_4]^-$	NSF_3
No. of substituents = 4 No. of lone pairs on Cl = 1 Shape: **Seesaw** (2)	No. of substituents = 4 No. of lone pairs on I = 2 Shape: **Square planar** (6)	No. of substituents = 4 No. of lone pairs on S = 0 Shape: **Tetrahedral** (1)

A mistake may be to assume that the lone pairs around Xe in $[XeF_3]^+$ occupy the two axial positions, leading to the incorrect molecular shape of trigonal planar.

AR9: Friendly Nitric Acid

Nitric acid can be made in the lab by reacting ammonium nitrate (NH_4NO_3) salt with dilute sulfuric acid (H_2SO_4) in a flask. The nitric acid is then isolated and collected via simple distillation. The reaction is as follows:

$$2NH_4NO_3 \text{ (s)} + H_2SO_4 \text{ (aq)} \rightarrow 2HNO_3 \text{ (aq)} + (NH_4)_2SO_4 \text{ (aq)}$$
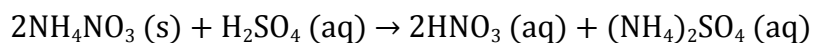
A chemist conducted an experiment and obtained a 25.0 cm^3 sample of nitric acid with a measured mass of 27.4 g. What is its concentration in mol dm^{-3}?

The density of water is 1 g cm^{-3}.

Leave your answer to 3 significant figures.

Solution:

1.52 mol dm^{-3}

$M_r(HNO_3) = 1.008 + 14.01 + 3(16.00) = 63.018$

Finding the concentration of the nitric acid solution obtained can be achieved by finding the amount of nitric acid dissolved in 25.0 cm^3 of water. The amount of nitric acid can in turn be found from the mass of the nitric acid component in the solution.

Mass of H$_2$O component $= 25.0$ g
Mass of HNO$_3$ component $= 27.4 - 25.0 = 2.4$ g

Amount of HNO$_3 = \dfrac{2.4}{63.018} = 0.038084$ mol (5 s.f.)

$\Rightarrow [HNO_3] = \dfrac{0.038084}{\frac{25.0}{1000}} = 1.52336$ mol dm^{-3} $= 1.52$ mol dm^{-3} (3 s.f.)

AR10: Radioactive, radioactive

"We knew the world would not be the same. A few people laughed, a few people cried. Most were silent."

- J. R. Oppenheimer

At the turn of the last century, physics took a dive into the subatomic, and its implications became hidden in murky waters. Despite the more invidious episodes of history which nuclear reactions have become associated with, the benefits that they brought upon mankind have stood the test of time.

An example of the improvements created by nuclear physics is the use of fission reactions in nuclear power plants, which provides about 10% of the world's energy demands today.

In a nuclear reactor, the following reaction occurs.

$$^{233}U + {}^{1}_{0}n \ \rightarrow \ A + {}^{137}Xe + {}^{3}_{0}n$$
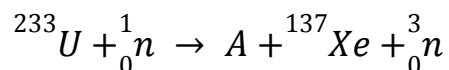
How many neutrons does particle **A** have?

Solution:

56

We know that the atomic number of Uranium, U is 92 while that of Xenon, Xe is 54. The reaction can be rewritten as

$$\prescript{233}{92}{U} + \prescript{1}{0}{n} \rightarrow A + \prescript{137}{54}{Xe} + \prescript{3}{0}{n}$$
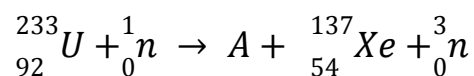
From the Law of Conservation of Mass, the total number of protons or neutrons at the start of the reaction must be equal to the total number of protons or neutrons at the end of the reaction.

The rest of the solution is an exercise in balancing the number of protons and nucleons.

Number of nucleons:
$$233 + 1 = (\text{Mass number of } A) + 137 + 3$$
$$\Rightarrow \text{Mass number of } A = 233 + 1 - 137 - 3$$
$$= 94$$

Number of protons:
$$92 + 0 = (\text{Proton number of } A) + 54 + 0$$
$$\Rightarrow \text{Proton number of } A = 92 - 54$$
$$= 38$$

The particle with proton number of 38 is Strontium, Sr. The identity of **A** is $\prescript{94}{38}{Sr}$.

The number of neutrons which **A** has is $94 - 38 = 56$.

AR11: Jo the Dinoflagellate

Jo the dinoflagellate lives a quiet life in the warm waters of coral reefs, flapping its whip-like flagella in order to move around and obtaining its energy by photosynthesizing with its chloroplasts.

On a particularly sunny afternoon, Jo felt hungry and decided to make some food. Using some of the water stored in its body, which comes to exactly 25% of its body mass, along with dissolved CO_2 present in excess in its surroundings, Jo produced stoichiometric amounts of glucose as well as O_2 (which is expelled to its surroundings).

After preparing the meal, Jo wants to find out how much its mass has changed. Note that expelled O_2 does not contribute to Jo's mass.

Calculate the percentage increase in Jo's mass during this process.

The photosynthesis reaction is
$$6H_2O \text{ (l)} + 6CO_2 \text{ (g)} \rightarrow C_6H_{12}O_6 \text{ (s)} + 6O_2 \text{ (g)}.$$
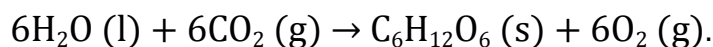
Leave your answer in 3 significant figures.

Solution:

16.7%

Let M be Jo's mass.

We know that the mass of water used in the photosynthesis reaction is 25% or $\frac{1}{4}$ of Jo's mass. Note that the change in Jo's mass is contributed only by the decrease in mass of water and the increase in mass of glucose, as CO_2 and O_2 are gases that are lost to the surroundings.

Mass of water reacted $= \frac{1}{4}M$

Amount of water reacted $= \dfrac{\frac{1}{4}M}{M_r(H_2O)} = \dfrac{\frac{1}{4}M}{2(1.008)+16.00} = \dfrac{1}{72.064}M$

As 6 mol water reacts to form 1 mol glucose,

Amount of glucose formed $= \dfrac{\frac{1}{72.064}M}{6} = \dfrac{1}{432.384}M$

$$\text{Mass of glucose formed} = \frac{1}{432.384}M \times M_r(C_6H_{12}O_6)$$
$$= \frac{1}{432.384}M \times [6(12.01) + 12(1.008) + 6(16.00)]$$
$$= \frac{180.156}{432.384}M$$

Final mass of Jo $= M - \frac{1}{4}M + \frac{180.156}{432.384}M = 1.16666M \, (6 \text{ s.f.})$

$\Rightarrow$ % increase in Jo's mass $= \dfrac{1.16666 - 1}{1} \times 100\% = 16.666\% = 16.7\% \, (3 \text{ s.f.})$

AR12: Vitamin B12

Vitamin B12, also called cobalamin, has the dubious distinction of being the most complex vitamin known to man (for good reason!). It took a collaboration between Eschenmoser and Woodward, two of the most eminent synthetic chemists of their time, to bring the only known formal total synthesis of this compound to fruition.
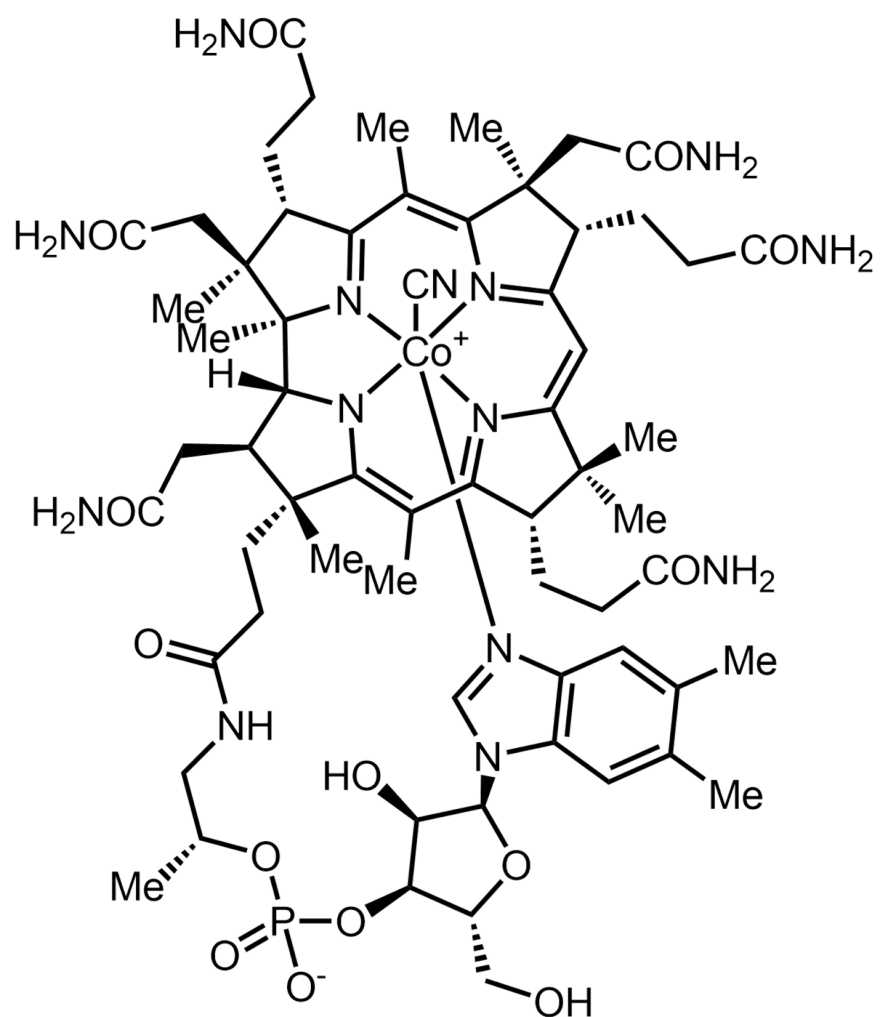
How many amide bonds are there in the structure of Vitamin B12?

Solution:

7

There are 6 $-CONH_2$ groups attached to the central corrin ring system as side chains, and one (sneaky) $-CONH$ group in the longest side chain.

AR13: Going green

In the hydrogen economy, hydrogen gas is transported under high pressure and used as fuel for various processes.

Suppose that H_2 gas is transported in a $70.0m^3$ container at a pressure of 500 bar, at 0^oC. Using this information and the following bond enthalpy values, give the amount of heat, in units of kJ, generated from the H_2 gas during its complete combustion.

Give your answer to 3 significant figures.

Bond	Bond enthalpy / kJmol^{-1}
C−C	+347
C−H	+413
O=O	+498
O−H	+464
C=O (in CO_2)	+805
C−O	+358
H−H	+436
C=C	+612

Solution:

374000000 kJ

Using n = PV/RT, we obtain the amount of H_2 gas stored:

$$n = \frac{PV}{RT} = \frac{(500 \times 10^5)(70.0)}{(8.3145)(273.15)} = 1.5411 \times 10^6 \, mol$$

By creating an energy cycle, we are able to obtain the enthalpy change of combustion of H_2:

$$\Delta H = \frac{1}{2} BE(O = O) + BE(H - H) - 2BE(O - H)$$
$$= -243 kJmol^{-1}$$

Thus, the total amount of heat released is $243(1.5411 \times 10^6) = 3.7449 \times 10^8$ kJ (5 s.f.) = 3.74 x 10^8 kJ, or 374000000 kJ (3 s.f.)

AR14: Hidden Information

Identify the type of stereoisomerism exhibited by the following molecule.
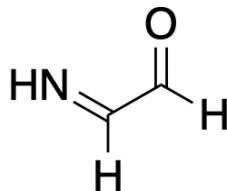
A) Enantiomerism
B) Diastereomerism
C) This molecule does not exhibit stereoisomerism

Input the letter corresponding to the correct choice. The answer is case-sensitive.

Solution:

B

or
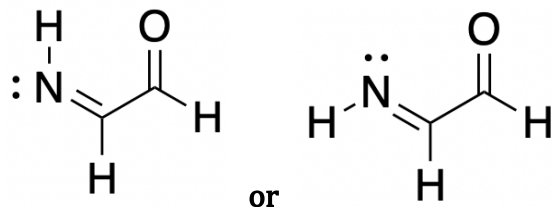
This is a form of cis/trans isomerism, or E/Z isomerism, which is a subset of diastereomerism. There is restricted rotation about the double bond of the imine (C=N) and there are two nonidentical groups on the doubly bonded N and C atoms, depending on whether the hydrogen attached to the imine is on the same side of the double bond as the aldehyde group.

AR15: Something doesn't add up…

Compound **A** is an interesting compound with two anions, and Ca^{2+} as the cation. **A** has calcium constituting 85.1% by mass of the compound. One of the anions is the nitride ion, N^{3-}.

Let the mass of the heavier anion be *a*, and the lighter anion be *b*. What is the value of a/b?

Leave your answer to 5 significant figures.

Solution:

25538

We can first start off by finding the molar mass of the compound. If calcium comprises 85.1% by mass of the compound, if the compound has one calcium atom, the molar mass is 40.08 / 0.851 = 47.1, which is very low and hence unlikely (no two anions make sense).

We can construct a list of the possible molar masses for the sum of the two anions:

$$7.02, 14.04, 21.06, 28.08, ...$$

Recalling that the compound should be electrically neutral, going beyond 4 calcium atoms (+8 charge) is unlikely. When we try out common anions, we find that 3 and 4 calcium atoms do not make too much sense (e.g. 28.08 likely corresponds to either 2 nitride anions with total -6 charge).

If the compound has two calcium atoms, the molar mass is 40.08 × 2 / 0.851 = 94.20. This means the combined mass of the two anions is 14.0. This looks oddly reminiscent of the nitride anion… but what could the other anion be? Ca_2N is not charge balanced, with a missing -1 charge. Could the other anion be… an electron? Yes, it is! The compound is in fact, an electride, $[Ca_2N]^+ e^-$.

So now we know the two anions, N^{3-} and e^-. We get that the N^{3-} anion has a relative atomic mass of 14.01, and using 1 amu = 1.6605×10^{-27} kg from the data sheet, we know that the mass of N^{3-} is $1.6605 \times 10^{-27} \times 14.01 = 2.3263605 \times 10^{-26}$ kg.

We also know the mass of an electron to be 9.1093×10^{-31} kg, also from the data sheet. Dividing their masses, we get $(2.3263605 \times 10^{-26}) / (9.1093 \times 10^{-31}) = 25538.30152 = 25538$ (5 s.f.).

AR16: Chad benzene

Imagine a series of hexagonal organic molecules made by interconnected benzene rings, where the next member has 1 more benzene ring on each side than the previous member. The 1st, 2nd and 3rd members are shown below:
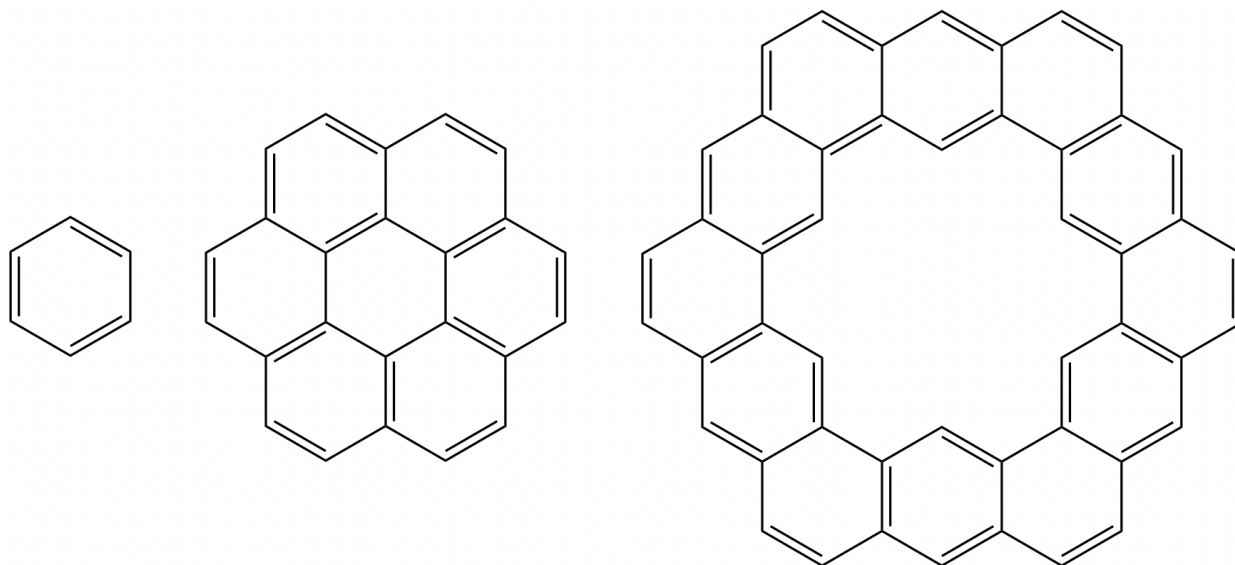
How many benzene rings would the 2023rd member have?

Solution:

12132

To solve this question we must derive a general rule for the number of benzene rings in the nth member of this series. As the nth member would have n rings on each side, but the rings found at the corners of the "superbenzene" are shared across 2 faces,

$$\text{Number of benzene rings} = 6n - 6 = 6(n-1)$$

Substituting n = 2023, we find $6(2022) = 12132$.

AR17: The Diversity of Life

Given the following 8 amino acids, how many different polypeptides of exactly 8 amino acids length can be formed?

Amino acids	Number of each amino acid available
Glycine	x3
Leucine	x2
Proline	x1
Hydroxyproline	x1
Phenylalanine	x1

Solution:

3360

The question, in effect, is asking us to permute the amino acids. Since peptides have directionality thanks to an N-terminus and a C-terminus, this is akin to ordering the amino acids from 1 to 8. Factoring in the repeated leucine and glycine units, we arrive at the expression:

$$^{8}P_8 \ / \ (2!)(3!) = 8! \ / \ (2!)(3!) = 3360$$

AR18: Destroyer of worlds

Congratulations; you've just won a free vacation to Los Alamos, New Mexico! State-of-the-art accommodation and delicious food indented! Naturally, you're not going to be allowed to leave until your work here is done. But you seem quite clever, so why not give it a shot?

Your colleague, Dr Leerstelle, has proposed a previously unknown chemical equation for the fission of Pu-239:

$$\,_{0}^{1}n \;+\; \,_{94}^{239}Pu \;\rightarrow\; \,_{39}^{96}Y \;+\; [\;\;] + \; 4\,_{0}^{1}n$$
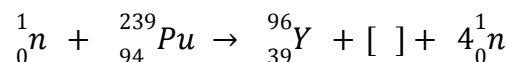
True to his name, Dr Leerstelle has left a blank space in his equation, and now wants you to help him fill it up. Oh Dr Leerstelle, you silly scientist! All he informs you is that the missing isotope is one of the following options:

A) $\,_{40}^{103}Zr$

B) $\,_{55}^{141}Xe$

C) $\,_{55}^{140}Xe$

D) $\,_{55}^{143}Xe$

E) $\,_{52}^{134}Te$

F) $\,_{41}^{102}Nb$

G) $\,_{55}^{140}Cs$

H) $\,_{55}^{139}Cs$

Furthermore, you've been assigned to find the multiplication factor k of this reaction, where:

$$k \;=\; \frac{Number\ of\ neutrons\ at\ the\ end\ of\ the\ reaction}{Number\ of\ neutrons\ at\ the\ start\ of\ the\ reaction}$$

When you present your solution to Dr Leerstelle, he wants it to be presented as the option letter representing the correct isotope followed by a 3-digit value of k (as if he's a computer trying to interpret your answer in a specific format).

For example, if your answer is that the isotope is $^{134}_{52}Te$ with the value of k being 173, your answer would be "E173".

If your answer is that the isotope is $^{103}_{40}Zr$ with the value of k being 17, your answer would be "A017".

(Reminder to never trust Dr Leerstelle with important research in the future.)

Solution:

G004

By comparing the atomic masses and atomic numbers on the left and right hand sides of the arrow, we can see that for our mystery isotope:
Mass Number $= 1 + 239 - 96 - 4 \times 1 = 140$
Atomic Number $= 94 - 39 = 55$

The element with atomic number 55 is Cs. Hence the isotope is $^{140}_{55}Cs$ (option G).

From the equation provided, the number of neutrons at the start of the equation is 1, and the number of equations at the end of the equation is 4. Hence:

$$k = \frac{Number\ of\ neutrons\ at\ the\ end\ of\ the\ reaction}{Number\ of\ neutrons\ at\ the\ start\ of\ the\ reaction} = \frac{4}{1} = 4$$

Since the isotope is $^{140}_{55}Cs$ with the value of k being 4, the answer is "G004".

AR19: A Pt-containing complex

Platinum (IV) chloride can combine with ammonia to form compounds. The coordination number of platinum in a particular complex with ammonia and chloride is 6. It is given that one formula unit of the compound contains a cation and 2 chloride counterions.

What is the number of ammonia ligands that are datively bonded to the platinum atom in the complex?

Solution:

4

Firstly, you need to deduce that the charge of the cation is +2. As Pt is present in its +4 oxidation state, this means that two of the 6 ligands bonded to Pt are chloride ions. This also means that the remaining 6 ligands must be ammonia.

AR20: The Tides of War

Phosgene was first deployed as a chemical weapon by the French, not the Germans in 1915 in World War I. It was also used in a mixture with an equal volume of chlorine, with the chlorine helping to spread the denser phosgene. Phosgene was more potent than chlorine, though some symptoms took 24 hours or more to manifest. Its structure is shown below.
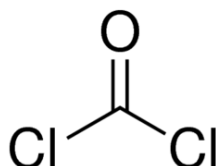
What is the ratio between the relative molecular mass of phosgene and the relative molecular mass of an acyl chloride moiety ($-COCl$)?

Let x be the Mr of phosgene and y be the Mr of the acyl chloride group. Give x/y to 3 significant figures.

Solution:

1.56

M_r of phosgene $= 12.01 + 16.00 + 2(35.45) = 98.91$

Acyl Chloride moiety is defined as –COCl, thus we only take into account these 3 atoms in the calculation.

Hence M_r of acyl chloride moiety $= 98.91 - 35.45 = 63.46$ (simply missing a Cl atom).

$\Rightarrow x : y = 98.91 : 63.46 = 1.56 : 1$ (3 s.f.)

AR21: Rocket candy!

There are three components needed to sustain a fire: a fuel, an oxygen source, and heat.

Jianhui understands this process and decides to make a mini firework at home with two household ingredients. Using fructose ($C_6H_{12}O_6$), as the fuel and potassium nitrate (KNO_3) as the oxygen source, Jianhui combines a small stoichiometric amount of each reagent in a ceramic dish to make the firework powder, and lights it on fire with a blowtorch.

The resulting vigorous combustion reaction produces potassium carbonate (K_2CO_3), carbon dioxide (CO_2), water vapour (H_2O), nitrogen gas (N_2), and a smile on Jianhui's face.

Satisfied with the results, Jianhui now wishes to recreate this experiment on a larger scale to impress a friend. Assume again that stoichiometric amounts of reactants are used. What is the mass of fructose needed, in grams, if Jianhui wants to make a 10g batch of firework powder?

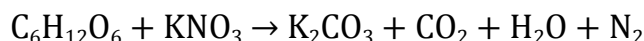*Leave your answer in 3 significant figures.*

Note: Do not attempt this experiment at home without proper protection and supervision.

Solution:

2.71 g

Firstly, with the information provided, we deduce a balanced equation for the reaction.

The unbalanced reaction is

$$C_6H_{12}O_6 + KNO_3 \rightarrow K_2CO_3 + CO_2 + H_2O + N_2$$

Balancing the reaction is tricky, so we can represent the coefficients for each reactant as some unknown m and n and solve for their values algebraically.

$$m\,C_6H_{12}O_6 + 2n\,KNO_3 \rightarrow n\,K_2CO_3 + (6m{-}n)\,CO_2 + 6m\,H_2O + n\,N_2$$
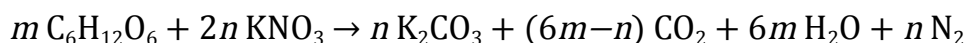
With respect to oxygen,
$$6m + 6n = 3n + 12m - 2n + 6m$$
$$\Rightarrow 12m = 5n$$

In order for all coefficients to be whole numbers, we let $m = 5$ and $n = 12$. This leaves us with
$$5C_6H_{12}O_6 + 24KNO_3 \rightarrow 12K_2CO_3 + 18CO_2 + 30H_2O + 12N_2$$
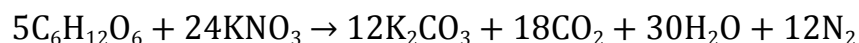
M_r of fructose, $C_6H_{12}O_6 = 6(12.01) + 12(1.008) + 6(16.00) = 180.156$
M_r of $KNO_3 = 39.10 + 14.01 + 3(16.00) = 101.11$

Assume Jianhui needs x grams of fructose.

Amount of fructose needed $= \frac{x}{180.156}$ mol

Stoichiometric amount of KNO_3 needed $= \frac{x}{180.156} \times \frac{24}{5}$ mol

Mass of KNO_3 needed $= (\frac{x}{180.156} \times \frac{24}{5} \times 101.11)$ g

Given that a total of 10g of reagents is needed,

$$\Rightarrow x + (\frac{x}{180.156} \times \frac{24}{5} \times 101.11) = 10$$
$$x(1 + \frac{1}{180.156} \times \frac{24}{5} \times 101.11) = 10$$
$$\Rightarrow x = 2.7071 \text{ g (5 s.f.)} = 2.71 \text{ g (3 s.f.)}$$
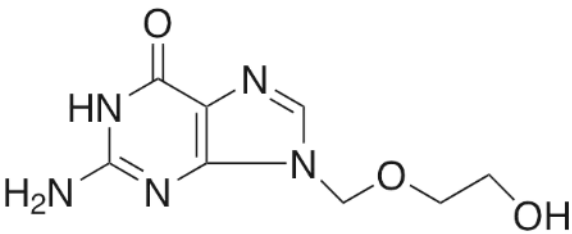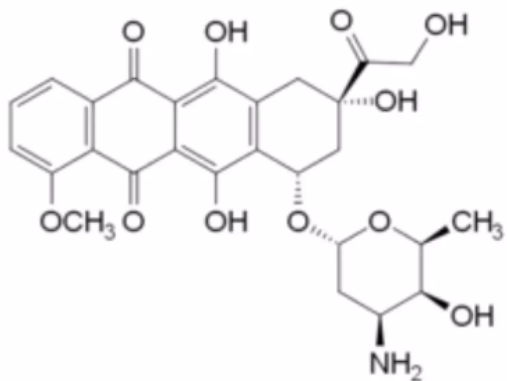
AR22: Lipinski's Rule of Five

Lipinski's rule of five is a concept frequently used in drug discovery. This rule helps to predict if a biologically active molecule is likely to have the chemical and physical properties to be orally bioavailable. In this question, we will consider only two of the rules. Lipinksi said that for a drug to have good oral bioavailability, it must possess:

1. No more than 5 hydrogen bond **donors** (A donor is a H atom bonded to an electronegative N, O or F atom).

2. No more than 10 hydrogen bond **acceptors** (A acceptor is an N, O or F atom with a free lone pair. Each atom is considered one acceptor.).

To be clear, a H_2O molecule has 1 hydrogen bond acceptor and 2 hydrogen bond donors.

How many of the drugs shown below obey the two rules of Lipinski?

	Acyclovir
	Doxorubicin

	Atorvastatin

Solution:

2

Acyclovir: 3 N−H bonds and 1 O−H bond (4 hydrogen bond donors); 8 N and O atoms in total (8 hydrogen bond acceptors) - Obeys Lipinski

Doxorubicin: 2 N−H and 5 O−H bonds (7 hydrogen bond donors); 12 O and N atoms in total (12 hydrogen bond donors) - Disobeys Lipinski

Atorvastatin: 3 O−H bonds and 1 N−H bond (4 hydrogen bond donors); 7 N and O atoms, 1 F atom (8 hydrogen bond acceptors) - Obeys Lipinski

AR23: Why So Negative?

There are several different electronegativity scales, each with their own advantages and limitations. One of the simplest and most widely used scales is the Pauling electronegativity scale:

Diagram 1: The Pauling Electronegativity Table

Suggest which of the following binary species have elements with the largest difference in electronegativity.
Input the number corresponding to the compound. Use Diagram 1 as reference.

1	2	3	4	5
TeI_2	SmI_2	N_2O_5	$[XeO_6]^{4-}$	GeH_4
5	6	8	9	10
SO_2	$AuCl_3$	UCl_6	$TlBr_3$	$NiSe$

Solution:

8

The calculated electronegativities are shown below.

1	2	3	4	5
TeI_2	SmI_2	N_2O_5	$[XeO_6]^{4-}$	GeH_4
0.56	1.49	0.40	0.84	0.19
5	**6**	**8**	**9**	**10**
SO_2	$AuCl_3$	UCl_6	$TlBr_3$	$NiSe$
0.86	0.62	<u>1.78</u>	1.34	0.64

AR24: Hock Hua Tonic?

Phenol and acetone are two important materials in many syntheses, and hence economical methods of producing these are important. The Hock process is a free radical reaction discovered by R. Ūdris and P. Sergeyev but named after Heinrich Hock (an example of Stigler's law[2] in action!) The general reaction scheme is provided below.
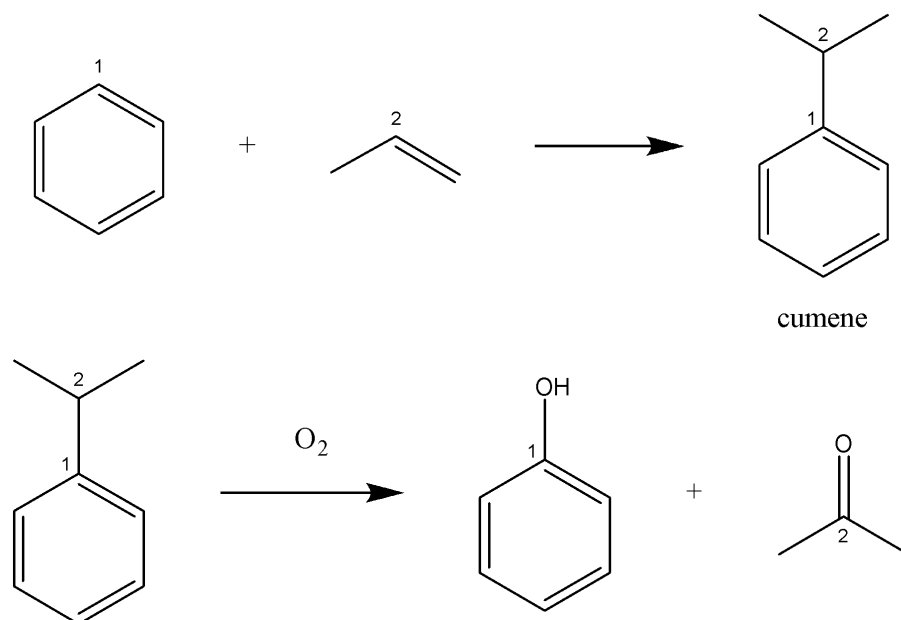
cumene

In the reaction, benzene reacts with propene first to produce cumene, which is then oxidised by oxygen gas to phenol and acetone.

During either of these steps, reduction and oxidation may occur. Find the sum of the changes in oxidation state to carbons 1 and 2 for each individual step.

*Key in your answer in the following format: <sum of changes in oxidation state in first step>,<sum of changes in second step> . For example, if the sum of changes in the first step and second step are 1 and 2 respectively, give your answer as **1,2**. Only give signs for negative changes.*

---

[2] Stigler's law states that "No scientific discovery is named after its original discoverer." For example, the Poisson distribution was described by Abraham de Moivre almost a century before Simeon Denis Poisson did so. In an exercise in irony, Stigler "borrowed" this law from Robert K. Merton's writings.

Solution:

1,4

For organic structures, it is often easiest to deduce oxidation states by considering what each carbon is bonded to. We first deduce the oxidation states relevant:
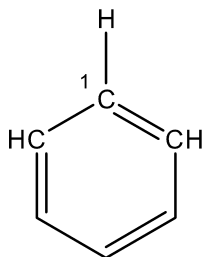
In benzene, carbon 1 has three bonds to other carbons and one bond to a more electropositive hydrogen, hence having an oxidation state of -1.
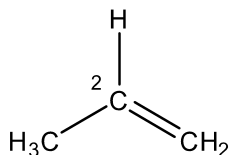
Similarly for propene, carbon 2 has three bonds to other carbons and one bond to a more electropositive hydrogen, hence having an oxidation state of -1.
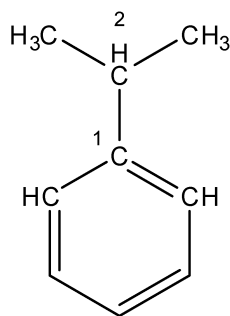
In cumene, carbon 1 is only bonded to other carbons and has an oxidation state of 0. Carbon 2 is bonded to three carbons and one hydrogen and has an oxidation state of -1. The changes of oxidation state in the first step are thus +1 and 0 (note that the carbon in propene undergoing redox in this step is actually the other end of the alkene, hence why the changes in oxidation state do not add to zero).
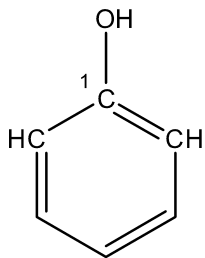
In phenol, carbon 1 has three bonds to carbons and one bond to a more electronegative oxygen, having an oxidation state of +1.
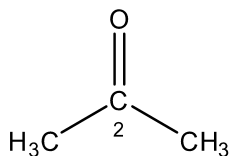
In acetone, carbon 2 is bonded to two carbons and doubly bonded to oxygen, having an oxidation state of +2. Hence, the changes of oxidation state in the second step are +1 and +3.

Hence, the total changes are +1 and +4, so we key in **1,4**.

AR25: Addition of sodium iodide to a solution containing Cu^{2+}

Give the formula of the precipitate formed when NaI (aq) is added to $CuSO_4$ (aq). Give your answer in the following format: For example, if your answer is sodium sulfate, key it in as: Na2SO4. If you think that no precipitate is formed, give your answer as: NIL

Solution:

CuI

Cu^{2+} and I^- react in a redox reaction to form CuI despite the fact that the overall cell potential at standard conditions is actually negative. This is because the precipitation of CuI (s) provides a powerful driving force for the reaction as it is highly insoluble, pushing the position of equilibrium of the reaction $2Cu^{2+}$ (aq) $+4I^-$ (aq) $\rightarrow 2CuI$ (s) $+ I_2$ (aq) to the right.

Possible incorrect answers are: CuI_2, NIL

AR26: Easy one (I promise)

Consider the following reaction:

$$CH_3CH{=}CH_2 + HBr \rightarrow ?$$
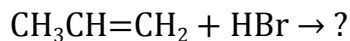
Which of the following statements is true regarding the reaction mechanism and stereochemistry?

A) The reaction involves a free radical, and the product is a racemic mixture of enantiomers.
B) The reaction proceeds via an electrophilic addition mechanism, and the product is a single enantiomer.
C) The reaction proceeds via a nucleophilic substitution mechanism, and the product is a racemic mixture of enantiomers.
D) The reaction proceeds via an electrophilic addition mechanism, and the product is a mixture of isomers.

Input the letter corresponding to the correct choice. The answer is case-sensitive.

Solution:

D

A simplified mechanism for the above reaction is as shown:
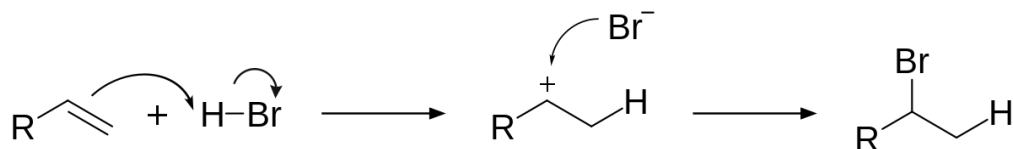
A) The reaction involves a free radical, and the product is a racemic mixture of enantiomers.

This statement is **incorrect.** The given reaction involves an alkene ($CH_3CH=CH_2$) reacting with HBr, which proceeds via an electrophilic addition mechanism, and involves ions instead of free radicals.

B) The reaction proceeds via an electrophilic addition mechanism, and the product is a single enantiomer.

This statement is **incorrect.** While the reaction proceeds via an electrophilic addition mechanism, the product formed when an asymmetrical alkene (like $CH_3CH=CH_2$) reacts with HBr is a mixture of structural isomers; $CH_3CH_2CH_2Br$ and $CH_3CHBrCH_3$.

C) The reaction proceeds via a nucleophilic substitution mechanism, and the product is a racemic mixture of enantiomers.

This statement is **incorrect.** Since the partially positive H atom in HBr is attacked by the electron-rich C=C double bond in $CH_3CH=CH_2$, HBr serves as an electrophile, not a nucleophile. Thus, the mechanism is electrophilic, not nucleophilic. Furthermore, the reaction is an addition reaction and not a substitution reaction.

D) The reaction proceeds via an electrophilic addition mechanism, and the product is a mixture of isomers.

This statement is **correct.** The given reaction involves an alkene ($CH_3CH=CH_2$) reacting with HBr, and it proceeds via an electrophilic addition mechanism. The product formed is bromopropane, and it exists as a mixture of geometric isomers ($CH_3CH_2CH_2Br$ and $CH_3CHBrCH_3$) depending on which carbon the H atom bonds to after the electrophilic attack.

AR27: The most royal of all!

Aqua regia (literally "regal water") is a combination of nitric and hydrochloric acid, mixed in a 1:3 ratio[3]. It was so named because of its ability to dissolve gold, according to the following equation:

$$Au + 3HNO_3 + 4HCl \rightleftharpoons [AuCl_4]^- + 3NO_2 + H_3O^+ + 2H_2O$$

Astute observers may have noticed that this is, in fact, a redox reaction. Several students commented on the reaction, as below:

Ammie: The oxidising agent is chlorine.
Metthew: Gold is being oxidised.
Walter: Nitrogen is reduced in the reaction.
Timmy: Gold is the reducing agent.
Brenny: This is a disproportionation reaction.
Bobo: The oxidation state of gold has increased from 0 to +5.

How many of the students' statements are correct?

---

[3] The correct ratio of nitric acid to hydrochloric acid in aqua regia is 1:3; this ratio has since been updated in the question. Knowledge of the ratio of reactants does not affect the solving of the problem.

Solution:

3

The correct statements are in green while the incorrect ones are in red. Explanations are as shown:

Ammie: The oxidising agent is chlorine.
The oxidation state of chlorine remains the same as it is -1 in both HCl and $[AuCl_4]^-$. Thus it does not act as an oxidising agent.

Metthew: Gold is being oxidised.
The O.S of gold has increased from 0 in Au to +3 in $[AuCl_4]^-$.

Walter: Nitrogen is reduced in the reaction.
The O.S of nitrogen has decreased from +5 in HNO_3 to +4 in NO_2.

Timmy: Gold is the reducing agent.
Gold has reduced nitrogen. Remember, the reducing agent is itself oxidised, and the oxidizing agent is itself reduced.

Brenny: This is a disproportionation reaction.
A disproportionation reaction is one where the same element is both oxidised and reduced. That has not happened in this case.

Bobo: The oxidation state of gold has increased from 0 to +5.
The O.S of gold has increased from 0 in Au to +3 in $[AuCl_4]^-$.

AR28: TDI

TDI is an organic compound with the formula $CH_3C_6H_3(NCO)_2$. Two of the six possible isomers are commercially important: 2,4-TDI (CAS: 584-84-9) and 2,6-TDI. 2,4-TDI is produced in the pure state, but TDI is often marketed as 80/20 and 65/35 mixtures of the 2,4 and 2,6 isomers respectively.

It is produced on a large scale, accounting for 34.1% of the global market in 2000, second only to MDI. Approximately 1.4 billion kilograms were produced in 2000. All isomers of TDI are colourless, although commercial samples can appear yellow. The structure of 2,4-TDI is shown below.
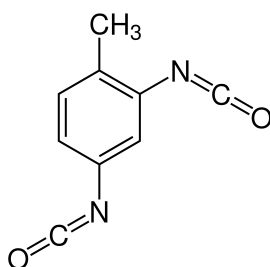
During its production, another organic compound, 2,6-TDI, is often found in the reaction mixture. 2,4-TDI and 2,6-TDI are isomers of each other. Between them, which type of isomerism is exhibited? Choose the *best* option below.

A) Cis-trans isomerism.
B) Enantiomerism
C) Fac-Mer isomerism.
D) Skeletal isomerism.
E) Positional isomerism.
F) Functional group isomerism.

Solution:

E

The $-NCO$ groups are connected at different carbons in the two isomers of TDI. Options A and B are subsets of stereoisomers, which is not correct because there is a different connectivity of atoms here.

Fac-Mer isomerism most often arises in coordination complexes.

Skeletal isomerism refers to differing connectivity of carbon atoms, which does not apply here as the carbon skeleton remains the same.

Nor are functional groups any different, thus functional group isomerism is not the answer.

AR29: The Energetics of Organic Reactions

The propagation steps of free-radical bromination of $(CH_3)_3CH$ can be expressed by the following reactions:

$$\text{Step 1: } (CH_3)_3CH + Br\cdot \rightarrow (CH_3)_3C\cdot + HBr$$
$$\text{Step 2: } (CH_3)_3C\cdot + Br_2 \rightarrow (CH_3)_3CBr + Br\cdot$$
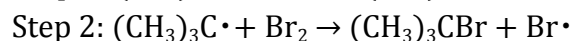
All steps involve homolytic fission.

Using the following bond energy values, calculate the overall enthalpy change of the reaction.
Leave your answer to 3 significant figures, in units of kJ mol^{-1}.

Bond	BE / kJmol^{-1}	Bond	BE / kJmol^{-1}
C−Br	276	Br−Br	193
C−H	413	H−Br	366

Solution:

-36.0 kJmol⁻¹

In step 1: A C−H bond is broken, while a H−Br bond is formed. Thus the enthalpy change of step 1 works out to be $BE(C-H) - BE(H-Br) = +47.0$ kJmol⁻¹.

In step 2: A Br-Br bond is broken, while a C−Br bond is formed. Thus the enthalpy change of step 1 works out to be $BE(Br-Br) - BE(C-Br) = -83.0$ kJmol⁻¹.

The overall enthalpy change works out to be -36.0 kJmol⁻¹.

AR30: Elemental Disagreements

You, a teacher, has just asked a few young chemistry enthusiasts to research on their favourite element and give a short class presentation on why they have chosen it as their favourite element. Full of zest and spirit, they each turn up to class the next day and proudly present the fruits of their labour.

Ammie: *Carbon is found in group 14 of the periodic table. I love it because it's the element of life. It's the most commonly occurring element in our body - not by mass, but by number of atoms! Relative atomic mass is also defined with respect to the carbon-12 isotope, which makes it extra-special for me.*

Metthew: *Ammie, how can it be that your favourite element is not iron? It's found in group 8. Just like the other group 8 elements ruthenium and osmium, it can achieve an incredible +8 oxidation state! And if that's not surprising enough, it's also very very important to life because it's what allows haemoglobin to bind to oxygen atoms.*

Walter: *My fellow chemists, I must passionately disagree. Surely iodine is the most fascinating element. It exists as the binary compound, I_2. It's also the only halogen that sublimates at room temperature and pressure - how special is that? When you perform the starch test, I_3^- is also the chemical species responsible for the blue-black colouration due to its complexation with starch.*

Nathaniel: *Hey, hey, let me have my say. My favourite element is sulfur! This is because it's in group 16, like oxygen, but it's more colourful! It also usually exists as S_2, which makes me wonder why we can't breathe in sulfur like how we breathe oxygen. Plus, it's also one of the most electronegative elements - only O, F and Cl are more electronegative on the Pauling scale!*

While the enthusiasm is to be much lauded, you can't help noticing that there are a few factually incorrect statements made, and you are quick to spot them.

How many factually incorrect statements did the 4 students make in total? One complete sentence is counted as one statement.

Solution:

4

Ammie: *Carbon is found in group 14 of the periodic table. I love it because it's the element of life.* It's the most commonly occurring element in our body - not by mass, but by number of atoms! (Going by the number of atoms, hydrogen would be more abundant!) *Relative atomic mass is also defined with respect to the carbon-12 atom, which makes it extra-special for me.*

Metthew: *Ammie, how can it be that your favourite element is not iron? It's found in group 8. Just like the other group 8 elements ruthenium and osmium,* it can achieve an incredible +8 oxidation state, even in stable compounds! (Iron unfortunately is only able to reach +7 oxidation state in its compounds. Fe(VIII) has only been observed to exist in transient intermediates.) *And if that's not surprising enough, it's also very very important to life because it's what allows haemoglobin to bind to oxygen atoms.*

Walter: *My fellow chemists, I must passionately disagree. Surely iodine is the most fascinating element. It exists as the binary compound, I_2. It's also the only halogen that sublimates at room temperature and pressure - how special is that? When you perform the starch test, I_3^- is also the chemical species responsible for the blue-black colouration due to its complexation with starch.*

Nathaniel: *Hey, hey, let me have my say. My favourite element is sulfur! This is because it's in group 16, like oxygen, but it's more colourful!* It also usually exists as S_2 (sulfur exists in many allotropes, but certainly not S_2 due to the poor overlap of the p orbitals discouraging double bond formation), *which makes me wonder why we can't breathe in sulfur like how we breathe oxygen.* Plus, it's also one of the most electronegative elements - only O, F and Cl are more electronegative on the Pauling scale! (nitrogen is also more electronegative.)

AR31: Addition Discrimination

When fuming sulphuric acid reacts with alkenes, addition reactions occur.

Explain why benzene does **not** undergo addition reactions with fuming sulphuric acid. Choose the *best* answer below.

A) Benzene is a bulky molecule and thus poses steric hindrance to any reactant seeking to perform an addition reaction.

B) Benzene is too inert to undergo addition reactions. The presence of activating and/or electron donating groups is recommended for addition reactions.

C) Benzene is resonance stabilised which renders it resistant to addition reactions which would destroy its aromaticity and make it less stable.

D) Both benzene and fuming sulphuric acid are acidic. Thus, no reaction will occur.

Solutions:

C

Option C is the best answer.

Benzene isn't considered particularly bulky (ruling out option A).

Inertness is a weak argument in explaining why addition reactions cannot react in the same way as substitution reactions, as increased activation energy is the main issue here (hence option B is wrong).

Benzene is hardly soluble in water, and hence does not really have a pH, since pH is normally used to describe aqueous conditions. As it is not really a Bronsted-Lowry base or acid, option D is invalid.

AR32: One Sandwich, Please[4]

In 1973, the Nobel Prize Committee must have been feeling really hungry. Perhaps they were even craving a PB&J, since they awarded the prize in chemistry to Ernst Otto Fischer and Geoffrey Wilkinson for their work in discovering "sandwich" compounds. These compounds consist of a metal bonded to two entire molecules, not just to one atom as one may expect. A classic example of sandwich compounds is ferrocene with the formula $Fe(C_5H_5)_2$. The structure of ferrocene is given below.
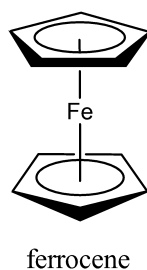
ferrocene

Ferrocene's discovery and its extra stability sparked a wave of interest in organometallic chemistry. To further understand ferrocene, we must first synthesise it. Consider the synthetic pathway below (note that equations may not be balanced fully):

ferrocene
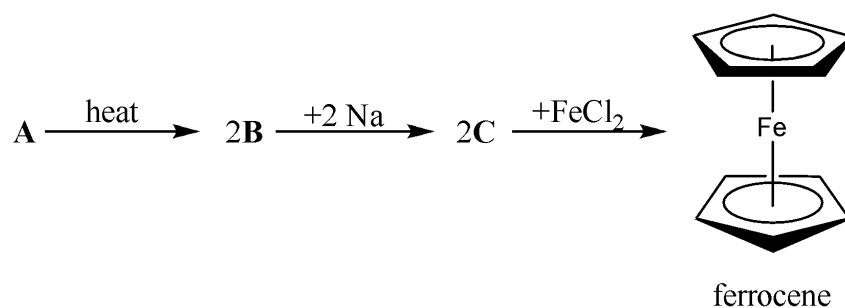
Give the structure of compound **A**. (Do not include any stereochemistry in your structure).

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[4] It was brought to our attention during the competition that many teams were unable to submit their solutions online. All teams who provided their solutions via Discord have had their marks updated accordingly.

Solution:
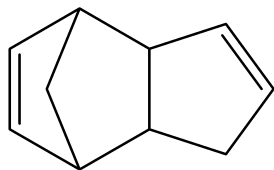
The full reaction scheme is as follows.
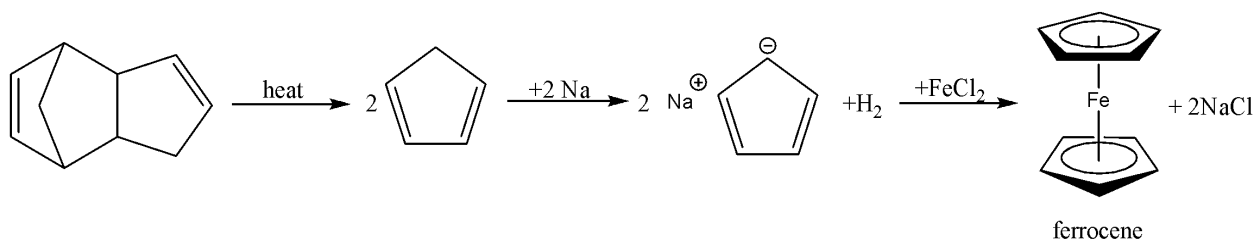
In the first step, the dimer A is heated and undergoes a retro-Diels Alder reaction to form 2 equivalents of cyclopentadiene B. B then undergoes a redox reaction with sodium to form sodium cyclopentadienide C which releases hydrogen gas. Finally, C reacts with iron(ii) chloride to form ferrocene.

AR33: Oil of Vitriol

*O'Brien did not speak. Two other voices were speaking. After a moment Winston recognized one of them as his own. It was a sound-track of the conversation he had had with O'Brien, on the night when he had enrolled himself in the Brotherhood. He heard himself promising to lie, to steal, to forge, to murder, to encourage drug-taking and prostitution, to disseminate venereal diseases, to throw **vitriol** in a child's face. O'Brien made a small impatient gesture, as though to say that the demonstration was hardly worth making. Then he turned a switch and the voices stopped.*

- *1984, George Orwell*

In the old days, sulphuric acid was known as oil of vitriol. Sulphuric acid has numerous applications in synthetic and surface chemistry, with millions of tonnes being manufactured industrially each year.

Benzene reacts with concentrated sulphuric acid in this manner.

The reaction is given as :

$$H_2SO_4 \; + \; SO_3 \; \rightleftharpoons \; H_2S_2O_7 \; (Oleum)$$

$$H_2S_2O_7 \rightleftharpoons HSO_4^- \; + \; HSO_3^+$$
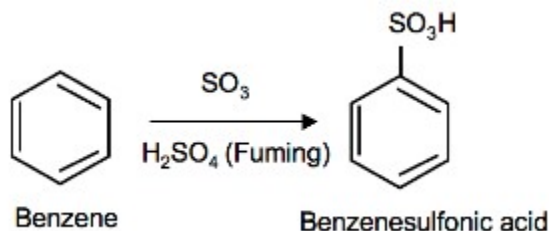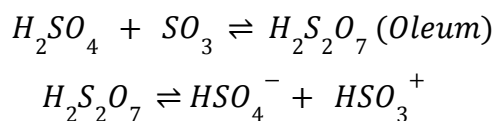
Which of the following shows the correct intermediate carbocation formed in the reaction? *Input the letter corresponding to the correct choice.*

A	B	C	D

Solution:

D

Analogous to how benzene attacks a positively charged halogen during halogenation by electrophilic substitution, we can draw the mechanism for attack on the $[SO_3H]^+$ ion as follows:
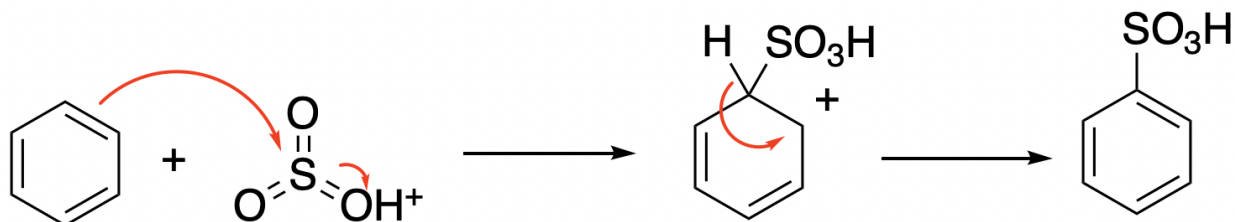
While some teams may be more familiar with seeing the + charge adjacent to the carbon bonded to the electrophile, it is important to remember that delocalisation of this + charge leads to multiple resonance structures, one of which is depicted in D.

AR34: I'm a Dazzle[5]

On March 7th, A new compound nicknamed 'I'm a Dazzle' was discovered on the planet Bogbelo. The nickname sounds similar to the name of an actual molecule on Earth, opined Bogbeloian scientists. In addition, it is identical in structure.

Phosgene ($COCl_2$) can react with one equivalent of 'I'm a Dazzle' to form this product.
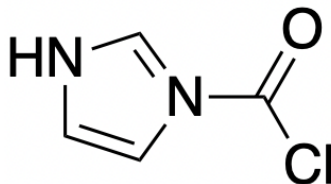
Draw the structure of 'I'm a Dazzle'.

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[5] It was brought to our attention during the competition that teams were unable to access this question on the platform. This question has been voided for SChL 2023.

Solution:
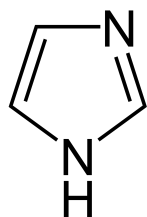
I'm a Dazzle = Imidazole

The structure can be deduced from recognizing the condensation reaction that undergoes between the two products, in the following manner:
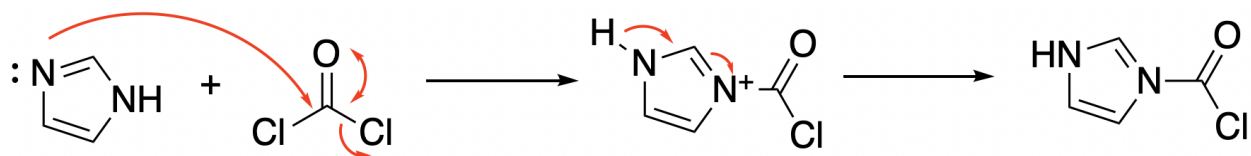
Side note: Strictly speaking, the first reaction should be split into two steps: A nucleophilic attack to form a tetrahedral carbon intermediate and an elimination step where a Cl⁻ ion is kicked out. However, for the sake of brevity, nucleophilic acyl substitution mechanisms are often condensed as such.

AR35: Feeling a little lonely

Lone pairs often tend to go unnoticed by beginner chemists and over-complacent veterans alike, despite the role they play in determining molecular geometry and resonance. Thus, let's refresh our basics with some lone-pair counting.

Cephalosporin C is a molecule found in a class of antibiotics called the cephalosporins, which share structural similarities with the universally recognised penicillin.
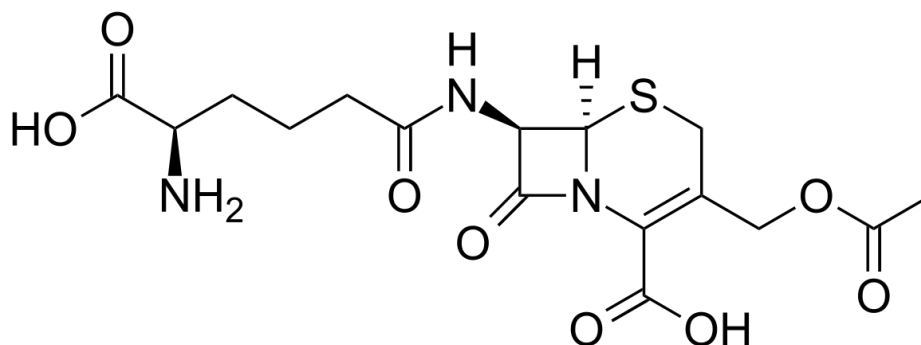
The structure of cephalosporin C

At physiological pH, how many lone pairs are there in one molecule of cephalosporin C?

Solution:

22

Under physiological conditions, the following ionisations will occur:

$-COOH \Rightarrow$	$-COO^-$
$-NR_3 \Rightarrow$	$-NHR_3^+$

However, esters are not protonated, and neither are the nitrogen atoms in amides, thanks to the resonance delocalisation of the lone pairs making them much weaker bases. Neither are thioether (R-S-R) groups, which are less basic than the OH^- ion.

A way to verify this experimentally is to pull up the pKa values of cephalosporin C, which turn out to be 2.6, 3.1 and 9.8, as expected of the presence of 2 carboxylic acid groups and a primary amine.

With that in mind, cephalosporin will ionise as follows:
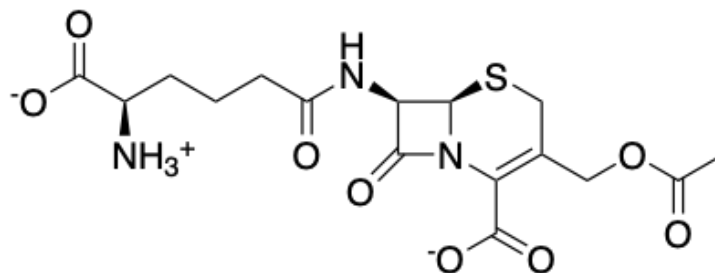
Each oxygen with 2 bonds bears 2 lone pairs, while each oxygen with a negative charge (and thus only 1 bond) bears 3. The sulfur atom, being in the same group as the oxygen atom and thus exhibiting analogous chemistry, bears 2 lone pairs. Each nitrogen bears 1 lone pair, except for the quaternary nitrogen on the primary amine, which bears no lone pairs. The lone pairs are visualised below:
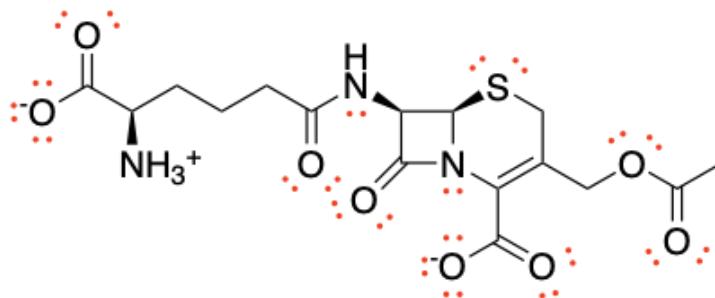
Thus, the sum works out to $2(3) + 6(2) + 2(1) + 2 = 22$.

AR36: Acromelobinic Acid Synthesis

This question is based on syntheses from acromelobinic acid's derivatives. The 2 reactants are subject to prolonged heating with concentrated sulfuric acid.

Which of the following is the **most likely** product of the reaction below? Assume that only **intermolecular** reactions occur.

Input the letter corresponding to the correct choice. The answer is case-sensitive.

C)

D)
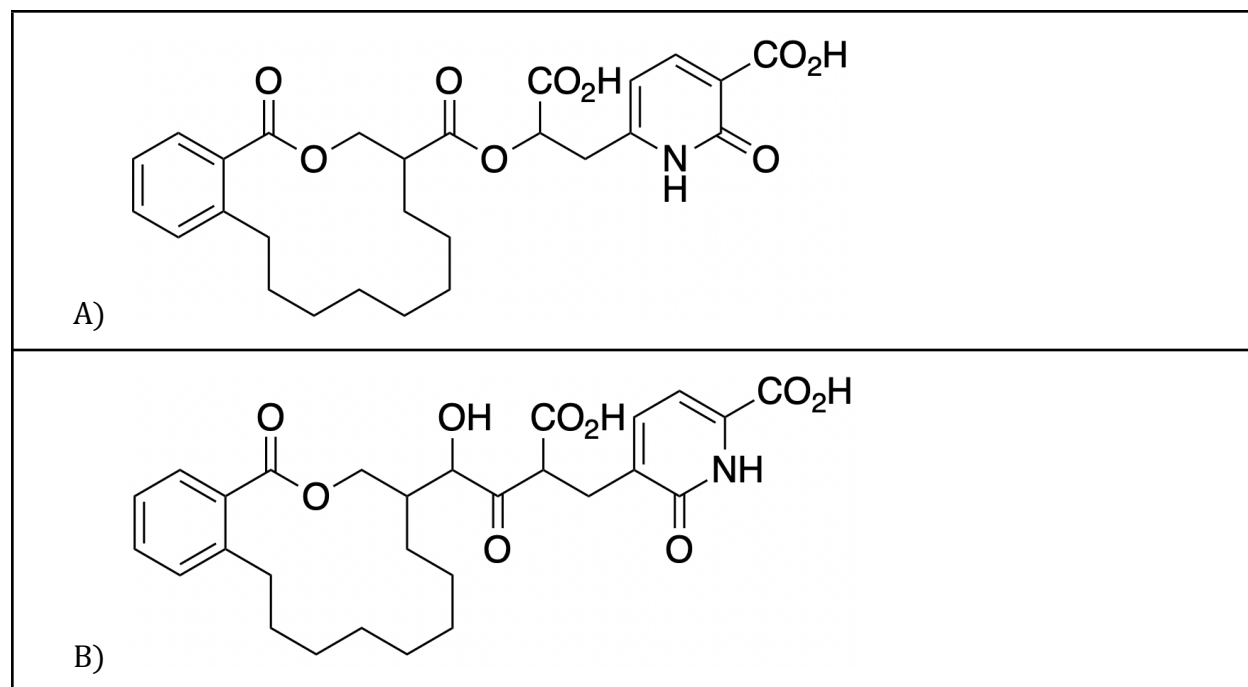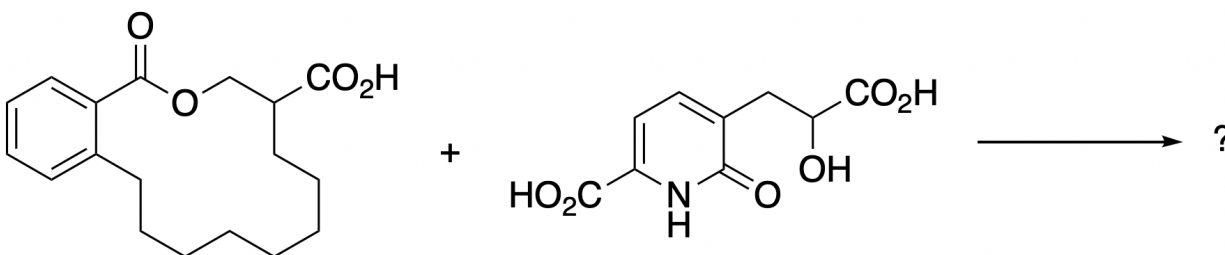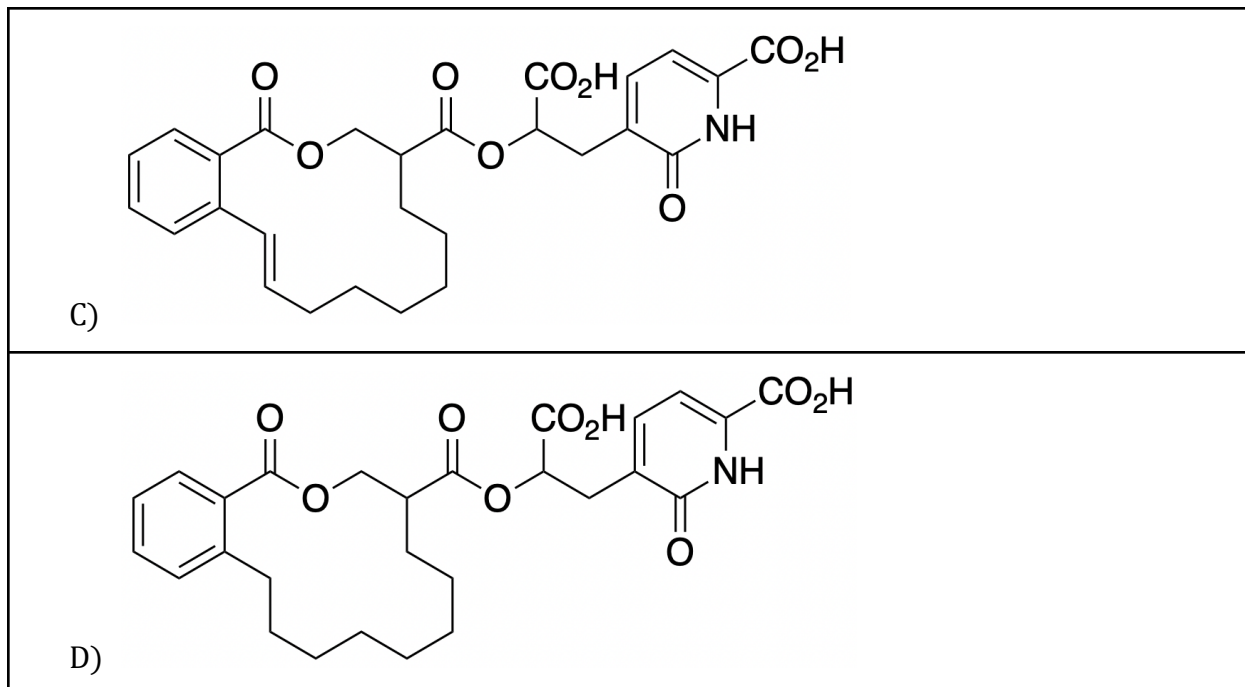
Solution:

D

Under the harsh conditions, esterification is almost guaranteed, which is the reaction of the carboxyl group in the first reactant with the hydroxyl group of the second reactant.

Option A is wrong because the amide in the second ring should be in swapped positions.

Option B is wrong since the ester linkage is flipped around.

Option C is wrong as there is an extra double bond in the non-aromatic multi-membered ring.

AR37: Drop Everything Now

Bobo has to conduct titration experiments for his chemistry practical. In this practical, he wants to find an unknown concentration of sodium ethanedioate. Bobo's practical worksheet is attached below.

You are provided with the following solutions:
FA1 is a solution containing an unknown concentration of $Na_2C_2O_4$.
FA2 is a solution containg 0.0200 mol dm^{-3} of $KMnO_4$.

Procedure
1. Fill the burette with **FA2**.
2. Pipette 25.0 cm^3 of **FA1** into a conical flask.
3. Place the thermometer into a conical flask and heat the conical flask over a Bunsen burner until the temperature exceeds 70°C.
4. Run 1 cm^3 of **FA2** into the conical flask. Swirl the conical flask until all pink colour disappears.
5. Continue adding **FA2** solution using the burette, swirling when necessary, until one drop of solution turns the solution in the conical flask from colourless to light pink. This is the end-point.
6. Record your titration results in a suitable table.

Results

Titration	1	
Final burette reading / cm^3	27.05	0:00
Initial burette reading / cm^3	0.00	
Total volume of FA2 used / cm^3	27.05	
Titration used (✓)	✓	

Calcul...

Concentration of $C_2O_4^{2-}$ in FA... 0.05 = 0.0542 mol dm^{-3}. (3s.f.)

Unfortunately, it seems Bobo spilled some permanganate on his practical worksheet. Is it possible for you to help him figure out what his second titration result was?

If it is possible, key in the titration result in the appropriate precision in units of cm³. If not possible, key in 0.

Solution:

27.10 cm^3

Amount of $C_2O_4^{2-}$ used $= 0.0542 \times \frac{25.0}{1000} = 0.001355$ mol

The balanced equation for the redox reaction between $C_2O_4^{2-}$ and MnO_4^- is shown below:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
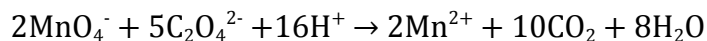
Amount of MnO_4^- used $= 0.001355 \text{ mol} \times \frac{2}{5} = 0.000542$ mol

Volume of FA2 used $= \frac{0.000542}{0.0200} \times 1000 = 27.10 \text{ cm}^3$.

At first, it seems that we can conclude that the titration reading is 27.15 cm^3. However, if the second reading is 27.10 cm^3 (and the averaged result is 27.08 cm^3), the result will be 0.05416 cm^3, which is more logical considering that the final result has been rounded to 3 s.f. We can eliminate 27.20 as that would be too far from the other result. Hence, 27.10 is the correct answer.

AR38: Flippy floppy

The following amide is reduced by LiAlH4.
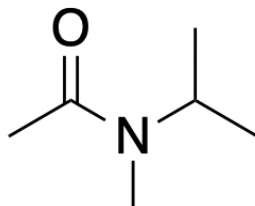
Suggest whether the product rotates plane-polarised light at room temperature and pressure.

Input Y for yes and N for no. The answer is case-sensitive.

Solution:

N

Amides are reduced to the corresponding amines by LiAlH$_4$:
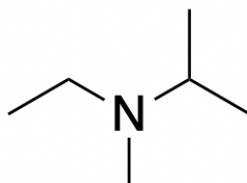
At room temperature and pressure, the temperature is sufficiently high for inversion at the nitrogen centre to occur, resulting in rapid flipping of the amine via a trigonal planar intermediate.

In effect this is similar to a racemic mixture of enantiomers, which does not rotate plane-polarised light.

AR39: Naming, Rearranging but with a Twist

Three isomers can be formed from sulfonation of toluene.

Isomer 1   Isomer 2   Isomer 3
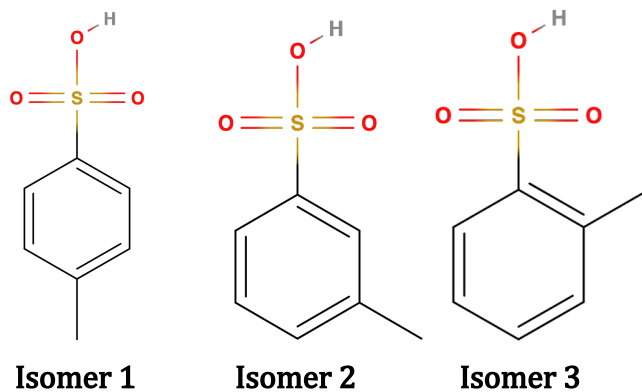
Arrange them in **increasing** order of theoretical concentration in the equilibrium. *If you believe the sequence is Isomer 1 < Isomer 2 < Isomer 3, give your answer as a single concatenated number 123.*

Solutions:

231

The order of increasing likelihood of formation is as follows:

meta-toluenesulfonic acid < ortho-toluenesulfonic acid < para-toluenesulfonic acid
(Isomer 2)   **(Isomer 3)**   **(Isomer 1)**
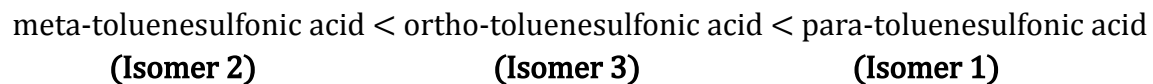
Methyl group is electron-donating, activating and 2,4-directing. Electrophile SO_3H^+ would be directed mainly to 2 and 4 (ortho and para) positions. Hence meta-toluenesulfonic acid is the most minor product. Ortho-toluenesulfonic acid would in theory be present in slightly lower concentration than para-toluenesulfonic acid due to steric hindrance of the bulky sulfonic acid ($-SO_3H$) group next to the methyl group.

AR40: Star anise

This is the structure of Jiadifenolide - a peculiar molecule which got its name from the native Chinese plant *Illicium jiadifengpi*, from which it was first isolated. Since its discovery, it has been a popular target for synthesis, due to its potential as a treatment for neurodegenerative diseases.
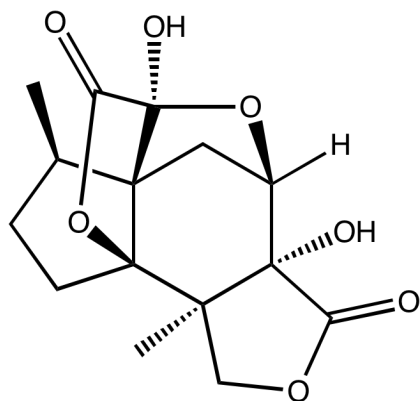
In the lab, a chemist mixes 1 mol of Jiadifenolide with an excess of dilute sodium hydroxide solution and heats the mixture under reflux.

The chemist then adds sodium metal to the reaction mixture *with no work-up step beforehand,* until no effervescence is observed. What is the amount of hydrogen gas, in moles, that is evolved?

Leave your answer to 1 d.p.

Solution:

2.0 mol

We understand from a knowledge of reagents and conditions that dilute sodium hydroxide with heating under reflux are conditions for alkaline hydrolysis.

This is useful because Jiadifenolide contains 2 cyclic ester groups (marked in red) which can be hydrolysed under these conditions.
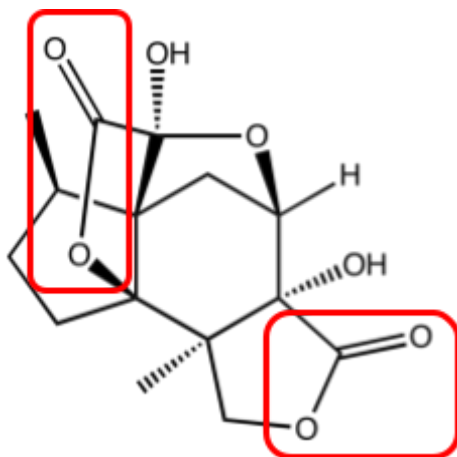
Hydrolysing these 2 ester bonds with NaOH (aq) produces the following structure.
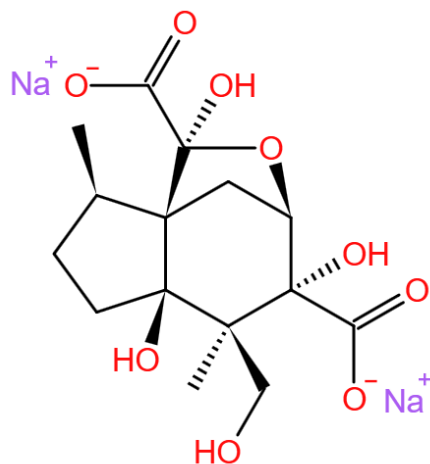
The resulting structure contains four alcohol groups which are able to react with Na metal. The reaction of one $-$OH group with Na metal produces 0.5 mol of H_2 gas.

$$R{-}OH + Na \rightarrow R{-}O^-Na^+ + \frac{1}{2}H_2$$
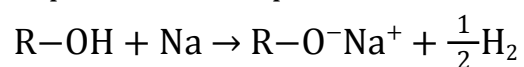
Hence, the reaction of 1 mol of jiadifenolide following alkaline hydrolysis produces 2 mol of H_2 gas.

AR41: A love letter to Lewis structure purists

Sulfur hexafluoride is usually represented with the Lewis structure shown below:
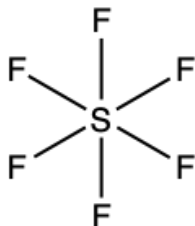
However, in reality it has been shown that sulfur only forms 4 full covalent bonds. How, then, to resolve this dilemma? The solution is simple: We can approximate the true Lewis structure of SF_6 with the following resonance structures, where an S^{2+} atom is covalently bonded to 4 fluorine atoms and two F^- ions are ionically bonded:
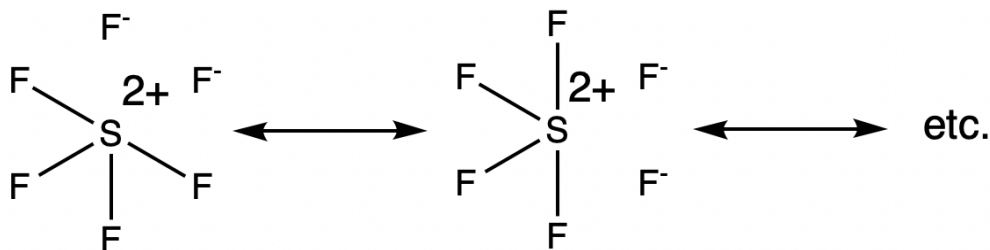
How many resonance structures does SF_6 have?

Solution:

15

What distinguishes each resonance structure from the other is *which 4 fluorine atoms* the S^{2+} ion is covalently bonded to. While it is possible to brute-force all possible structures, the wonders of combinations and permutations offer us a simple mathematical operation to solve the question:

$$^{6}C_{4} = 15$$

It is important to note that, while all 15 resonance structures are *structurally identical* to each other (each can be superimposed on the other by a rotation), they are still counted as distinct resonance structures. It is as if we have assigned the 6 fluorine atoms distinct numbers, from F_1 to F_6, so as to "lock" the orientation of the molecule in space.

AR42: Double it and pass it on

In biology, there is a rule of thumb that the rate of a reaction doubles for every 10°C increase in temperature. This rule is most commonly applied to enzyme-catalysed reactions, as most of its activation energies are similar in magnitude.

Two identical reaction setups are prepared. One reaction setup is placed on the benchtop at 25°C and the other in an oven at 35°C. The reaction at 35°C is later found to proceed twice as fast as the reaction at 25°C.

Find the activation energy of this reaction in kJ mol^{-1}.

Leave your answer in 3 significant figures. You may omit the + sign if your answer is positive.

Hint: The Arrhenius equation may come in handy.

Solution:

52.9 kJmol⁻¹

With identical starting reactant concentrations, the rate of the reaction depends on the magnitude of the rate constant, k. The rate constant changes depending on temperature, which is why increasing the temperature will increase the rate of reaction.

The relation between the rate constant and temperature can be found using the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

where A is the pre-exponential factor that describes the frequency of successful collisions (constant) and E_a is the activation energy of the reaction.

Letting k_{25} and k_{35} denote the rate constant at 25°C and 35°C respectively,

$$\frac{k_{35}}{k_{25}} = \frac{Ae^{-\frac{E_a}{R(273.15+35)}}}{Ae^{-\frac{E_a}{R(273.15+25)}}} = e^{\frac{E_a}{R(298.15)}-\frac{E_a}{R(308.15)}} = e^{\frac{E_a}{R}\left(\frac{1}{298.15}-\frac{1}{308.15}\right)}$$

Given that the rate at 35°C is twice the rate at 25°C, $\dfrac{k_{35}}{k_{25}} = 2$.

$$\Rightarrow e^{\frac{E_a}{R}\left(\frac{1}{298.15}-\frac{1}{308.15}\right)} = 2$$

$$\frac{E_a}{R}\left(\frac{1}{298.15}-\frac{1}{308.15}\right) = \ln 2$$

$$E_a = \frac{R\ln 2}{\frac{1}{298.15}-\frac{1}{308.15}} = \frac{(8.3145)\ln 2}{\frac{1}{298.15}-\frac{1}{308.15}}$$

$\Rightarrow E_a = 52949$ Jmol⁻¹ (5 s.f.) $= 52.9$ kJmol⁻¹ (3 s.f.)

AR43: The Universe is a Chaotic Place

The fundamental principle of a spontaneous reaction is that it must result in an increased entropy in the universe. The Gibbs free energy equation we are familiar with is simply another way to express this axiom. The equivalence can be shown as follows:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T} \text{ (at constant pressure)}$$

$$T\Delta S_{universe} = T\Delta S_{system} - \Delta H_{system}$$

$$-T\Delta S_{universe} = -T\Delta S_{system} + \Delta H_{system}$$

As by definition $\Delta G = \Delta H - T\Delta S$ at constant temperature, we conclude that for a spontaneous reaction, $\Delta G > 0$ because $\Delta S_{universe} < 0$ and $T > 0$.

The following data are given for a reaction taking place at 450K, under constant pressure.

ΔG	-10.4 kJmol^{-1}
ΔH	-45.0 kJmol^{-1}

What is the value of $\Delta S_{system} \times \Delta S_{surroundings}$?

Leave your answer to 5 significant figures, in units of J^2 mol^{-2} K^{-2}.

Solution:

-7688.9 J²mol⁻²K⁻²

From either personal knowledge or the derivation given above, it may be observed that $\Delta S_{\text{surroundings}} = -\dfrac{\Delta H_{system}}{T}$. Thus,

$$\Delta S_{\text{surroundings}} = -\frac{-45.0}{450} \text{ kJmol}^{-1}\text{K}^{-1}.$$

We can derive ΔS_{system} directly from

$$\Delta S_{\text{system}} = \frac{\Delta H_{system} - \Delta G}{T} = \frac{-45.0 + 10.4}{450} \text{ kJmol}^{-1}\text{K}^{-1}.$$

Thus,

$$\Delta S_{\text{system}} \text{ x } \Delta S_{\text{surroundings}} = \frac{-45.0 + 10.4}{450} \times -\frac{-45.0}{450} \times 10^6 = \text{-7688.9 J}^2\text{mol}^{-2}\text{K}^{-2}$$

AR44: Radiopharmaceuticals

The structure below shows the structure of pentetate indium disodium, or ^{111}In-DTPA (the cations are not shown for brevity). It is a mouse monoclonal antibody which is used for cancer diagnosis.
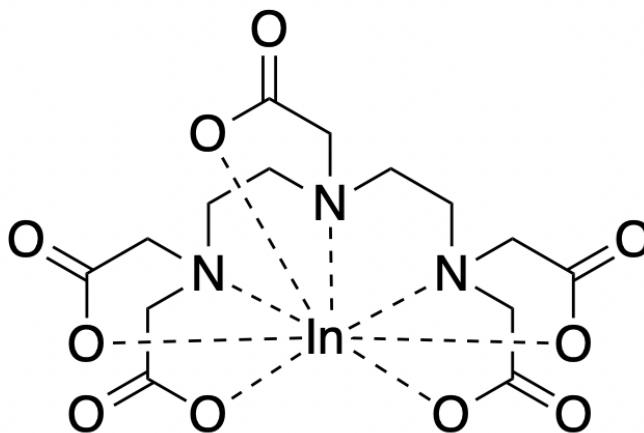
The ^{111}In atom decays in the body through electron capture.

Electron capture is a process where an atom absorbs an electron and emits a neutrino (with a small mass and zero charge).

What is the oxidation state of the In atom in ^{111}In-DTPA, and what is the oxidation state of the central atom in the decay product?

Denote an oxidation state of -x as 0x, an oxidation state of +x as 1x and an oxidation state of 0 as 00. Your answer will be the two numbers concatenated.

For example, if the oxidation state of the In atom in ^{111}In-DTPA is +1, and the oxidation state of the central atom in the decay product is -5, leave your answer as 1105.

Leave your answer a 4 digit number.

Solution:

1312

Notice that there are 5 singly negatively charged ligands in ^{111}In-DTPA (5 CO_2^- ligands), and the nitrogen-containing ligands are all neutral.

Since ^{111}In-DTPA is a disodium salt, we can deduce that the oxidation state of the In atom is $+5 - 2 = +3$.

When the ^{111}In atom decays via an electron capture mechanism, it becomes ^{111}Cd. The oxidation state of ^{111}Cd decreases by 1 to become $+2$.

Therefore, the answer is **1312**.

AR45: Please, take a seat

For most six-membered cyclic molecules, the structure with the lowest energy (i.e. the most stable structure) is the **chair conformation**. Other than cyclohexane (C_6H_{12}), the chair conformation can be adopted by compounds such as cyclo-hexasulfur (S_6) and hexasilabenzene (Si_6H_6).
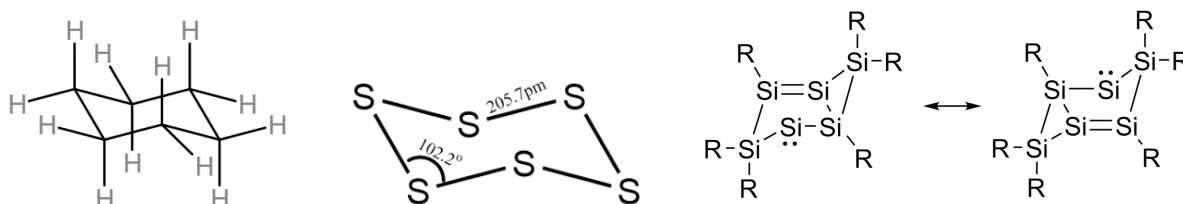
Figure 1: *Left - cyclohexane. Middle - cyclo-S_6. Right - an analogue of Si_6H_6*[6].

When three molecules of ethanal (CH_3CHO) react at room temperature in the presence of H_2SO_4, it produces a six-membered trimer called paraldehyde ($C_6H_{12}O_3$). Paraldehyde has the following skeletal structure, and adopts a chair conformation when most stable.
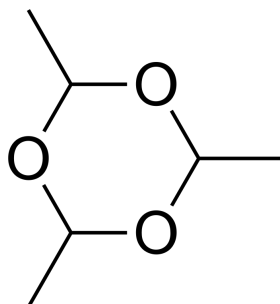
Depending on the orientation of the three methyl groups with respect to the ring, paraldehyde can exist in several different **configurations**. These configurations are unique, meaning that they are unable to interconvert between each other by means of ring flips or rotation about single bonds.

How many unique configurations does paraldehyde have?

Hint: Visualise the chair conformation in 3D to find out which configurations are unique, and which are actually the same configuration.

---

[6] Abersfelder, K., White, A. J. P., Rzepa, H. S., & Scheschkewitz, D. (2010). *A Tricyclic Aromatic Isomer of Hexasilabenzene. Science, 327* (5965), 564–566. doi:10.1126/science.1181771. Extracted from https://pubmed.ncbi.nlm.nih.gov/20110501/

Solution:

2

The 2 possible unique configurations are as shown. Every other possibility can be achieved via ring flip or bond rotation of these configurations.

(1)   (2)
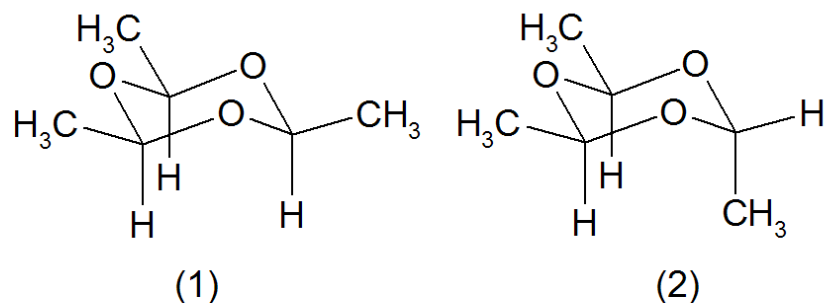
The two groups bonded to each atom on a six-membered ring can be classified as an axial or an equatorial group. Axial groups point above and below the ring, and equatorial groups point outwards from the hexagonal centre.

Axial groups   Equatorial groups
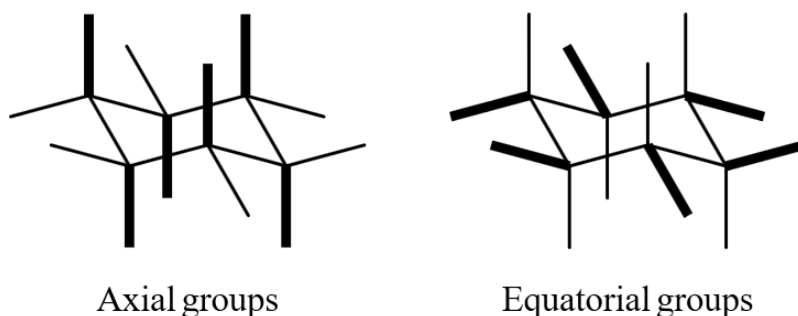
In paraldehyde, each carbon atom in the ring is bonded to one $-CH_3$ group. The $-CH_3$ group occupies either an axial or an equatorial position on the ring, hence we can label each of the three $-CH_3$ groups as axial or equatorial.

Due to the symmetry of the molecule, there are only 4 ways to label the three $-CH_3$ groups:
  (1) All $-CH_3$ equatorial
  (2) Two $-CH_3$ equatorial, one $-CH_3$ axial
  (3) One $-CH_3$ equatorial, two $-CH_3$ axial
  (4) All $-CH_3$ axial

These have the following chair structures respectively:

(1)   (2)   (3)   (4)
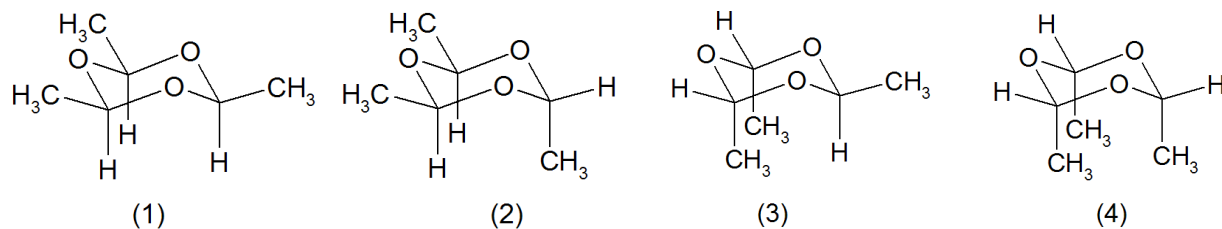
However, are there 4 different unique configurations? Recall that configurational isomers are isomers with different spatial arrangements of atoms, that cannot be achieved by rotation about single bonds or ring flips. Examples are cis-trans isomers (different arrangement of groups about a rigid double bond) and diastereomers (different arrangement of groups about a chiral centre).

Recall that a ring flip changes all equatorial groups to an axial group and vice versa. Therefore, for our paraldehyde structures, we can see that (1) and (4) are of the same configuration, because they can interconvert by means of a ring flip. Similarly, (2) and (3) can interconvert via a ring flip.
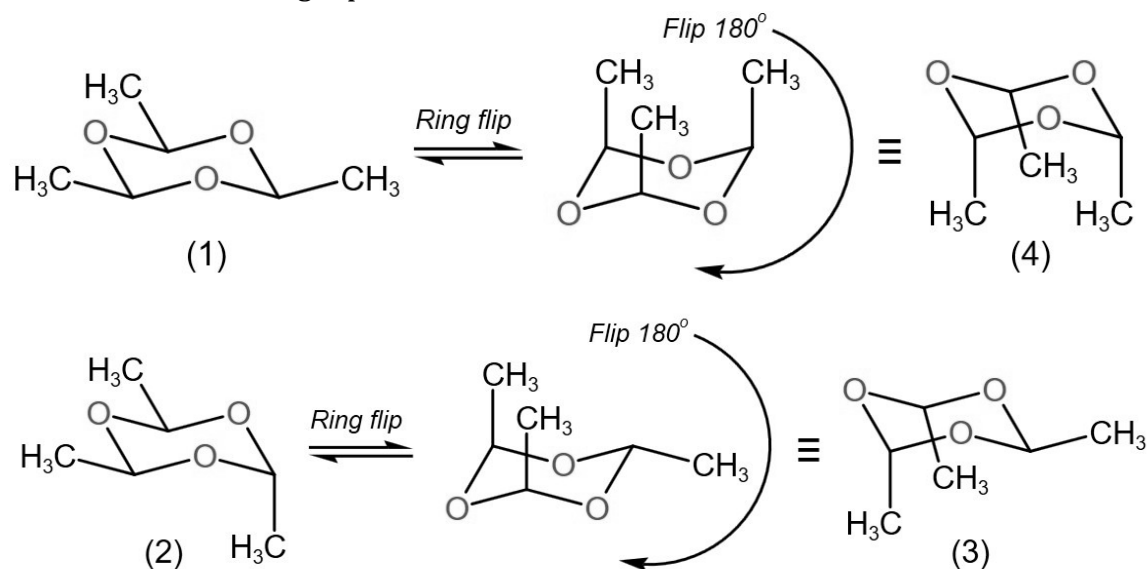
The preamble on chair conformation preempts solvers to think through the problem in terms of possible structures in a chair conformation. Another way that we can clearly visualise the 2 unique structures is by drawing these wedge-and-dash diagrams, where we see that considering the problem from a different perspective is much encouraged.

AR46: Iodoform Test

How many below would have a positive haloform test?

Leave your answer as a whole number.
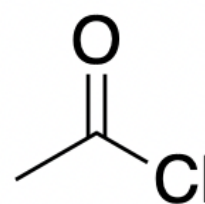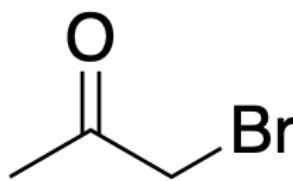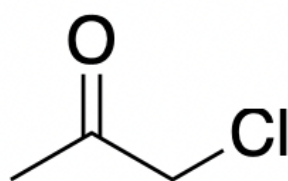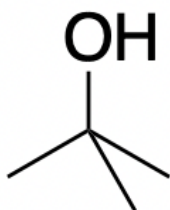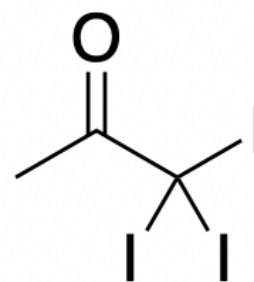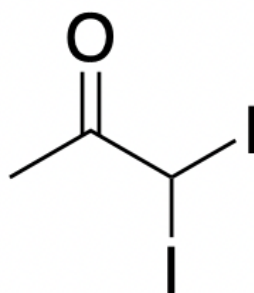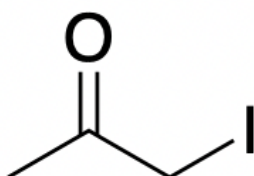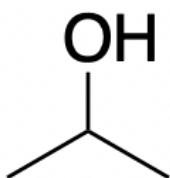
Solution:

6

The 6 molecules that yield a positive haloform test are:
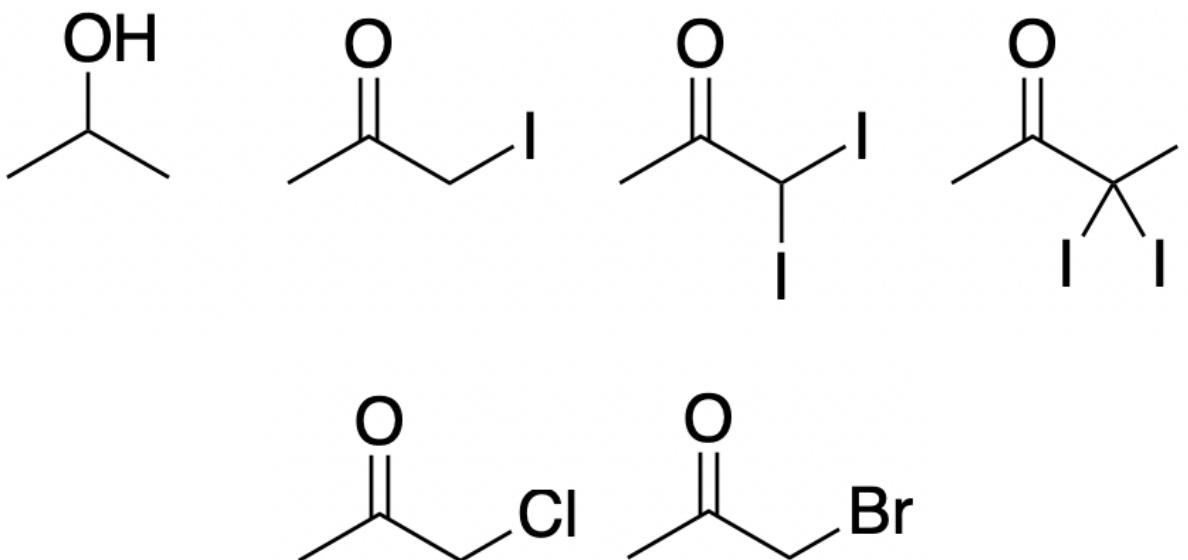
For the iodoform, or any haloform test to work, the conditions are that it must have a $-$ CHCH$_3$OH group or a ketone that contains at least one alpha hydrogen. This rules out tert-butanol. The mechanism is shown below:
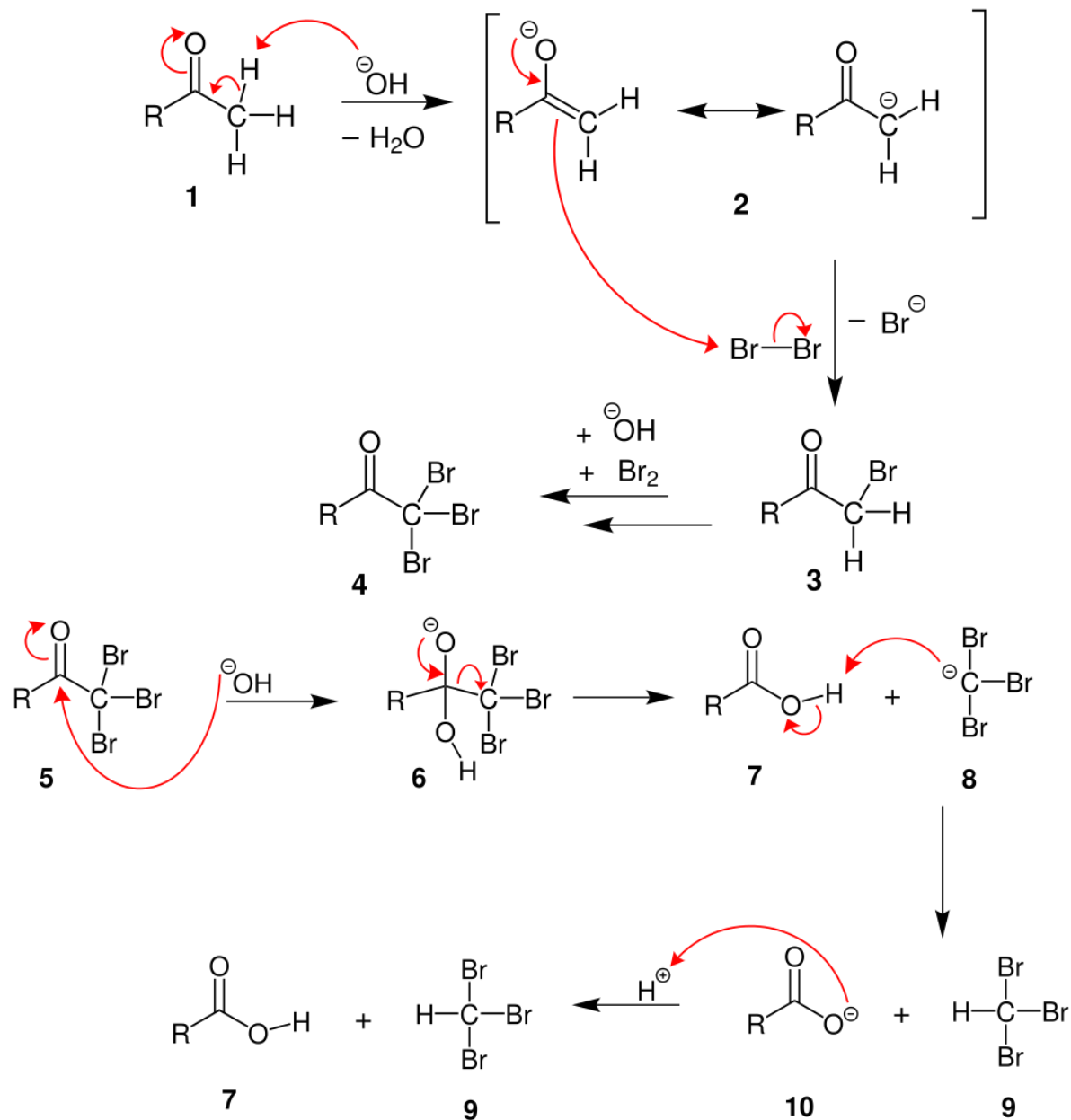
Any intermediate species should also, logically, be able to give a positive haloform test. In addition, it is worth noticing that while the mechanism shown above uses bromine as the halogen, the halogen is interchangeable between Cl, Br and I (with F being the only halogen that cannot be used).

Additionally, acyl halides are unable to give a positive haloform test as the aqueous conditions would cause it to hydrolyse.

AR47: That's Not Water

Liquid ammonia is able to dissolve many chemical compounds. Like water, liquid NH_3 undergoes autoionisation with an equilibrium constant $K_{am} = 5.1 \times 10^{-27}$ mol^2 dm^{-6}.

The pH scale measures the concentration of H^+ ions. In water, H^+ exists as H_3O^+. In liquid NH_3, H^+ exists as NH_4^+, so we may apply the concept of pH to liquid NH_3 as well.

A weak acid HR has a pK_a of 8.3 in NH_3(l). If 0.05 mol of NaR is dissolved in 100 cm^3 of liquid NH_3, find the pNH_4^+ of the resultant solution.

Leave your answer to 2 decimal places.

Solution:

17.14

Autoionisation of $NH_3(l)$:

$$2NH_3(l) \rightleftharpoons NH_2^-(am) + NH_4^+(am)$$
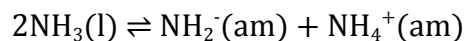
(where am means dissolved in aqueous ammonia)

$K_{am} = [NH_2^-][NH_4^+] = 5.1 \times 10^{-27}$

$pK_{am} = 26.29 = pNH_4^+ + pNH_2$

$pK_{am} = pK_a + pK_b$
$pK_b = pK_{am} - pK_a = 17.99$

$K_b = 10^{-17.99}$

Analogous to an aqueous solution, we can use the formula $[NH_2^-] = \sqrt{K_b C}$ (where C is the concentration of conjugate base R⁻), since the conjugate base is a weak base.

$[NH_2^-] = \sqrt{10^{-17.99} \times 0.5} = 7.15 \times 10^{-10}$ mol dm⁻³

$pNH_2 = 9.15$

Hence, $pNH_4^+ = 17.14$

AR48: Infinite Activation

Imagine a hypothetical reaction with an infinite number of elementary steps. For the nth step, $E_a = 50(0.5^{n-1})$ kJ mol^{-1}, and the energy difference between the transition state and the intermediate formed is $40(0.25^{n-1})$ kJ mol^{-1}.

What is the value of the enthalpy change that the overall reaction approaches, when expressed in kJ mol^{-1}?

Give your answer to 3 significant figures. If the enthalpy change is positive, omit the + sign.

Solution:

46.7 kJmol^{-1}

The enthalpy change of the nth step can be expressed as $50(0.5^{n-1}) - 40(0.25^{n-1})$. Thus, when this pattern progresses infinitely, the overall enthalpy change of the reaction approaches:

$$[50(0.5^0) - 40(0.25^0)] + [50(0.5) - 40(0.25)] + [50(0.5^2) - 40(0.25^2)] + \ldots$$
$$= 50[(0.5)^0 + (0.5)^1 + (0.5)^2 + \ldots] - 40[(0.25)^0 + (0.25)^1 + (0.25)^2 + \ldots]$$

As the general formula for the sum to infinity of a convergent series is $\frac{a}{1-r}$, where ar^{n-1} is the general formula for the nth term, the expression above simplifies to

$$= 50\left(\frac{1}{1-0.5}\right) - 40\left(\frac{1}{1-0.25}\right)$$
$$= 46.7 \text{ kJmol}^{-1} \text{ (3 s.f.)}$$

AR49: Couple How?

Phosgene fully reacts with 4 equivalents of imidazole to form Carbonyldiimidazole (CDI) which is used extensively in coupling in peptide synthesis. CDI's structure is shown below.
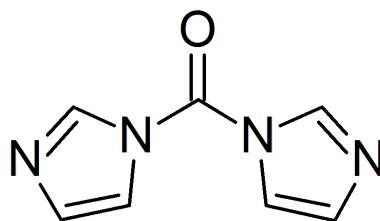
Jingliu, a medical student, is helping her consultant prepare a chemical reaction utilising CDI in creating a peptide. She draws up a reaction scheme shown below.
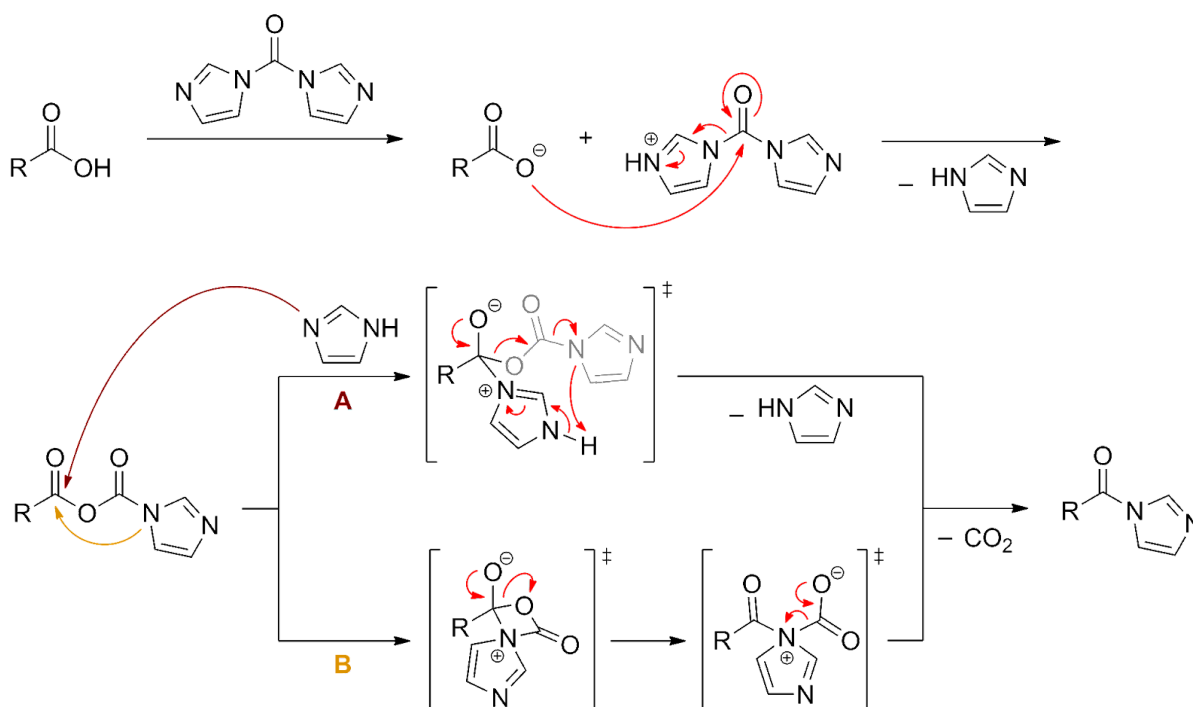
Jingliu has considered that there are 2 possible reaction pathways, A and B, but isn't sure which one is more favourable. She has generated 4 different thoughts in her head below.

Given that Jingliu uses a highly concentrated solution of imidazole as a starting reagent, which reaction pathway, A and B do you think is more favourable and why? Choose the *best* option below.

A) **Pathway A.** Reaction pathway B features the formation of a four membered ring that experiences much steric strain due to deviation from VSEPR bond angle. (~90° compared to 109.5°), thus it is unfavourable and requires high activation energy. Reaction pathway A in contrast has no such formation.

B) **Pathway B.** Reaction pathway B features the formation of a four membered ring that experiences much steric strain due to deviation from VSEPR bond angle. (~90° compared to 109.5°), thus the bonds are strained easily and easily broken, hence the rate of reaction is accelerated.

C) **Pathway A.** Intermolecular reactions are statistically more likely to happen compared to intramolecular reactions, hence another imidazole molecule is more likely to attack the starting product instead of the pre-existing imidazole moiety attacking the starting product.

D) **Pathway B.** Intramolecular reactions are statistically more likely to happen compared to intermolecular reactions, hence the pre-existing imidazole moiety is more likely to attack the starting product instead of another imidazole molecule.

Solution:

A

Option A is the best answer. The reaction that predominates is described by pathway **A**, the intermolecular mechanism involving nucleophilic attack of the ester carbon by a molecule of imidazole.

The key reason against pathway **B** is that the high activation energy required to form the four membered intermediate in pathway **B** outweighs any apparent increase in rate of reaction owing to steric strain, making it very unlikely for it to occur.

Mechanistic investigations by Staab and Maleck (1966)[7] showed additional kinetic considerations that favour pathway **A**. In addition to the unfavourable sterics of the intramolecular pathway **B** that involve the formation of the high-activation-energy 4-membered ring, the amide N atom that attacks the ester carbon in pathway **B** is much less nucleophilic due to delocalisation of its lone pair into the C=O bond, as compared to the N atom in imidazole which attacks the ester carbon in pathway **A**. This rules out options B and D, which are in favour of pathway **B**.

Although it is heavily implied in the question that there is a sufficiently high starting concentration of imidazole, making it much more likely for intermolecular reactions to occur, option C is also incorrect as intramolecular reactions are in reality statistically more likely to happen than intermolecular reactions.

Hence, option A is the most accurate.

[7] Staab, H. A., Maleck, G. (1966). *Über den Mechanismus der Reaktion von N.N′-Carbonyl-di-azolen mit Carbonsäuren zu Carbonsäure-azoliden, 99*(9), 2955–2961. doi:10.1002/cber.19660990931. Extracted from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cber.19660990931

AR50: Chem-mystery?

You and your team of expert pharmaceutical spies are tasked with obtaining the recipe of the top-selling drug from the headquarters of your main competitor company. This interesting compound has been used to treat nausea, watery eyes, cough, itching, as well as the common cold.

Sounds chemagical?

After combing through classified records on the compound, here is what you and your team have gathered:

(1) This neutral compound has a molar mass of 255 g mol^{-1} (3 s.f.).
(2) It contains 2 phenyl groups, bonded to the same carbon atom.
(3) It contains an N atom that is part of a tertiary amine.
(4) It contains an O atom that is not bonded to any H atom.
(5) There are 2 atoms between the O and the N atom in its structure.
(6) It does not contain any elements other than C, H, N and O.
(7) It has a plane of symmetry.

What is the structure of this mysterious compound?

Do not include the stereochemistry of the compound, if any.

Solution:
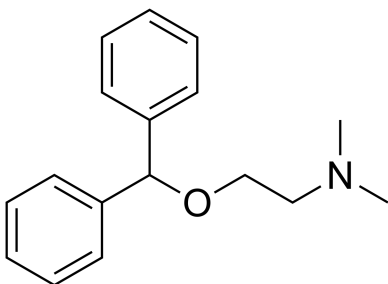
Based on the molar mass and the presence of certain functional groups, we can make deductions on the number of atoms of each element present.

The compound contains
  ● At least 13 C atoms (2 benzene groups, and the carbon connecting them)
  ● 1 N atom (1 tertiary amine)
  ● 1 O atom
which have a combined molar mass of 186 gmol⁻¹ when rounded to 3 s.f.

The remaining $255 - 186 = 69$ gmol⁻¹ is contributed by the C and H atoms not yet accounted for.

With trial and error, we see that the most probable molecular formula for the compound is **$C_{17}H_{21}NO$**. Due to the presence of the 2 benzene rings, the molecule has at least 8 degrees of unsaturation, which must be taken in account when confirming the molecular formula.

From (2), we confirm that the molecule contains the structure
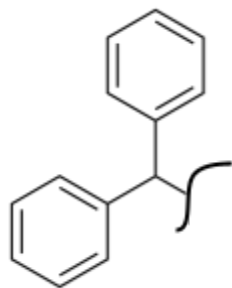
From (3), (4) and (5), the molecule also contains the structure
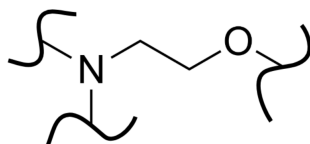
In order to satisfy the hydrogen deficiency index, the molecule must not contain any further rings or π bonds. From (7), two of the groups bonded to the amine N atom must be identical, and given the number of C atoms in the molecule, have to be methyl groups.
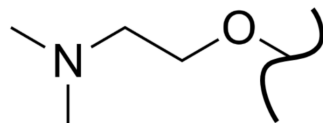
Joining the two fragments we have obtained together yields the mysterious molecule. The name of the molecule is diphenhydramine. It is commonly mixed in a 1:1 ratio with another compound, 8-chlorotheophylline, in the over-the-counter drug Dimenhydrinate.

AR51: Liquefied Emeralds

In the popular MMORPG Minecraft server, WynnCraft, the main currency used are liquefied emeralds.

Emeralds are a variety of the mineral beryl, with the formula $Be_3Al_2(SiO_3)_6$. However, real emeralds are hard to liquefy. Instead, they decompose at fairly low temperatures. The **unbalanced** equation is shown below:

$$Be_3Al_2(SiO_3)_6 \rightarrow SiO_2 + Be_2SiO_4 + BeAl_2O_4$$
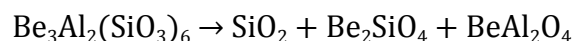
To determine the purity of 113.5 grams of emeralds, the emeralds were heated and fully decomposed. Next, SiO_2 was fully dissolved in excess HF, forming H_2SiF_6. Assume that the other compounds formed do not react with HF.

The amount of H_2SiF_6 was then determined by gravimetry. Excess $BaCl_2$ was added to the solution of H_2SiF_6, forming $BaSiF_6$. After filtering and weighing with a high precision electronic balance, the mass of the precipitate was 252.8663 grams.

What is the percentage purity (by mass) of the emerald sample (in %)?

Leave your answer to 2 d.p.

Solution:

86.07%

Number of moles of $BaSiF_6$ = $253.8663 \div (137.3 + 28.09 + 19.00 \times 6) = 0.908645$ mol

This is equal to the number of moles of H_2SiF_6, and equivalently the number of moles of SiO_2, since $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$.

Next, we need to determine the number of moles of $Be_3Al_2(SiO_3)_6$. We will start off by balancing the equation of the decomposition:

$$Be_3Al_2(SiO_3)_6 \rightarrow 5SiO_2 + Be_2SiO_4 + BeAl_2O_4$$
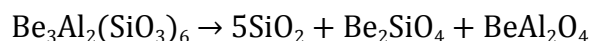
Hence, the number of moles of $Be_3Al_2(SiO_3)_6 = 0.908645 \div 5 = 0.181729$ mol

Mass of $Be_3Al_2(SiO_3)_6$ = $0.181729 \times (9.01 \times 3 + 26.98 \times 2 + (28.09 \times 3 + 16.00 \times 3) \times 6) = 97.684779$ grams.

Percentage purity = $97.684779 \div 113.5 \times 100\% =$ **86.07%**.

AR52: Salt and vinegar

Curious Bren notices that dissolving a small amount of purple potassium permanganate crystals in a solvent of concentrated sulfuric acid yields a remarkable green solution.

What could the green solution be made of? Bren is interested to find out, and called up four good friends to discuss this problem together. They each came up with one balanced chemical equation, predicting the products of the irreversible reaction.

(1) $KMnO_4 + H_2SO_4 \rightarrow K^+ + HMnO_4 + HSO_4^-$
(2) $2KMnO_4 + 3H_2SO_4 \rightarrow 2K^+ + Mn_2O_7 + H_3O^+ + 3HSO_4^-$
(3) $KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_4SO_3H + H_3O^+ + 2HSO_4^-$
(4) $KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^-$
(5) $KMnO_4 + 2H_2SO_4 \rightarrow K^+ + H_2MnO_4^+ + 2HSO_4^-$

To find out which equation is the most accurate, Bren decides to use a constant called the **cryoscopic constant (K_f)**:

$$K_f = \frac{R \cdot M \cdot T_f^2}{\Delta_{fus} H}$$

- R is the ideal gas constant,
- M is the molar mass of the solvent in kg mol^{-1},
- T_f is the freezing point of the pure solvent in K,
- $\Delta_{fus} H$ is the molar enthalpy of fusion of the solvent in J mol^{-1}.

The purpose of this K_f value is that it allows Bren to find the **van't Hoff factor, i.** It is related to K_f through the equation:

$$K_f = - \frac{\Delta T_f}{i \cdot b}$$

- ΔT_f is the freezing point depression, which is the change in freezing point of a solvent after the solute is added in K,
- i is the van't Hoff factor. It is important because it gives the number of product particles that is formed when one formula unit of $KMnO_4$ dissociates in H_2SO_4.
- b is the molality of the solution in mol kg^{-1}.

Bren finds that in one particular study, $KMnO_4$ is dissolved in pure concentrated H_2SO_4 forming a solution with 0.00365 mol kg^{-1} molal concentration of $KMnO_4$. This action caused the freezing point of the H_2SO_4 to decrease from 10.310 °C to 10.175 °C.

It is given that H_2SO_4 has a $\Delta_{fus}H$ value of 10.71 kJ mol^{-1}.

Which of the above equations describes the most likely reaction that occurs?
If you believe the correct option is (1), input your answer as "1". If you believe it is option (2), input your answer as "2" and so on.

Solution:

4

This question may look long and hard to digest. However, after understanding the purpose of the equations and plugging in the data provided, we can find the van't Hoff factor of the reaction quite quickly.

We find K_f using the first equation, then substitute it in the second equation to find i.

M_r of $H_2SO_4 = 2(1.008) + 32.06 + 4(16.00) = 98.076$
T_f of $H_2SO_4 = 10.31\ ^\circ C = 283.46\ K$

$$\Rightarrow K_f = \frac{R \cdot M \cdot T_f^2}{\Delta_{fus}H} = \frac{(8.3145)(\frac{98.076}{1000})(283.46)^2}{(10.71)(1000)} = 6.1178\ kgKmol^{-1}\ (5\ s.f.)$$

$\Delta T_f = 10.175 - 10.31 = -0.135\ ^\circ C = -0.135\ K$ (note the $-$ sign since T_f decreases)

Hence,

$$i = -\frac{\Delta T_f}{K_f \cdot b} = -\frac{-0.135}{(6.1178)(0.00365)} = 6.0457\ (5\ s.f.) = 6\ \text{(nearest integer)}$$

As the van't Hoff factor is close to 6, it implies that the most likely reaction that happens involves 1 formula unit of $KMnO_4$ dissociating to form 6 product particles. This is consistent only with **equation (4)**.

$$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^-$$
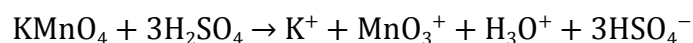
This method of extracting information about the reaction and reactants depending on how the freezing point of the reaction mixture changes from the pure solvent is called cryoscopy, which is based on freezing point depression: the property that the freezing point of a solvent decreases when an impurity is added to it. If this sounds familiar, it is the same principle behind ice melting more easily when salt is poured on it.

The specific reaction of $KMnO_4$ with H_2SO_4 was investigated by Royer, D. J. (1960)[8], which was the inspiration for this problem.

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[8] Royer, D. J. (1960). Evidence for the existence of the permanganyl ion in sulphuric acid solutions of potassium permanganate. *Journal of Inorganic and Nuclear Chemistry*, *17*(1-2), 159–167. doi: 10.1016/0022-1902(61)80202-9. Extracted from https://www.sciencedirect.com/science/article/abs/pii/0022190261802029

AR53: Make-a-ligand

The compound below is a common chelating agent for alkaline earth metals as a pentadentate ligand.
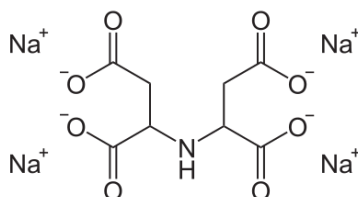
This ligand can be fairly easily synthesised:
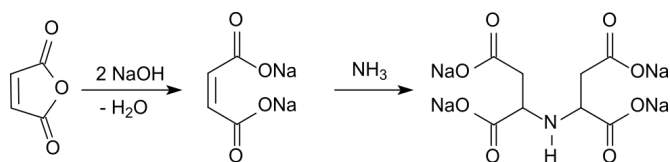
In the synthesis above, how many stereoisomers of the final product will be formed? .

Leave your answer as a number.

Solution:

3

There are two chiral centres in the molecule, but the (R, S) and (S, R) products are identical as it is a meso compound. This leaves us with 3 stereoisomers.

AR54: Based

The Cannizzaro reaction is an interesting reaction, in which an aldehyde disproportionates to form an alcohol and a carboxylate under basic conditions. An example reaction equation is shown below:
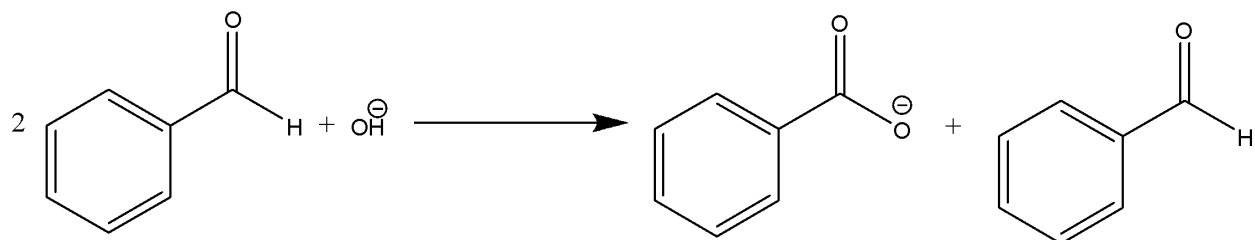
The kinetics of the Cannizzaro are especially interesting. It is found that the reaction is always second order with respect to the aldehyde, but what is especially interesting is that the reaction is initially first order with respect to OH⁻ but becomes second order at high base concentrations. This is explained with the following simplified mechanism:
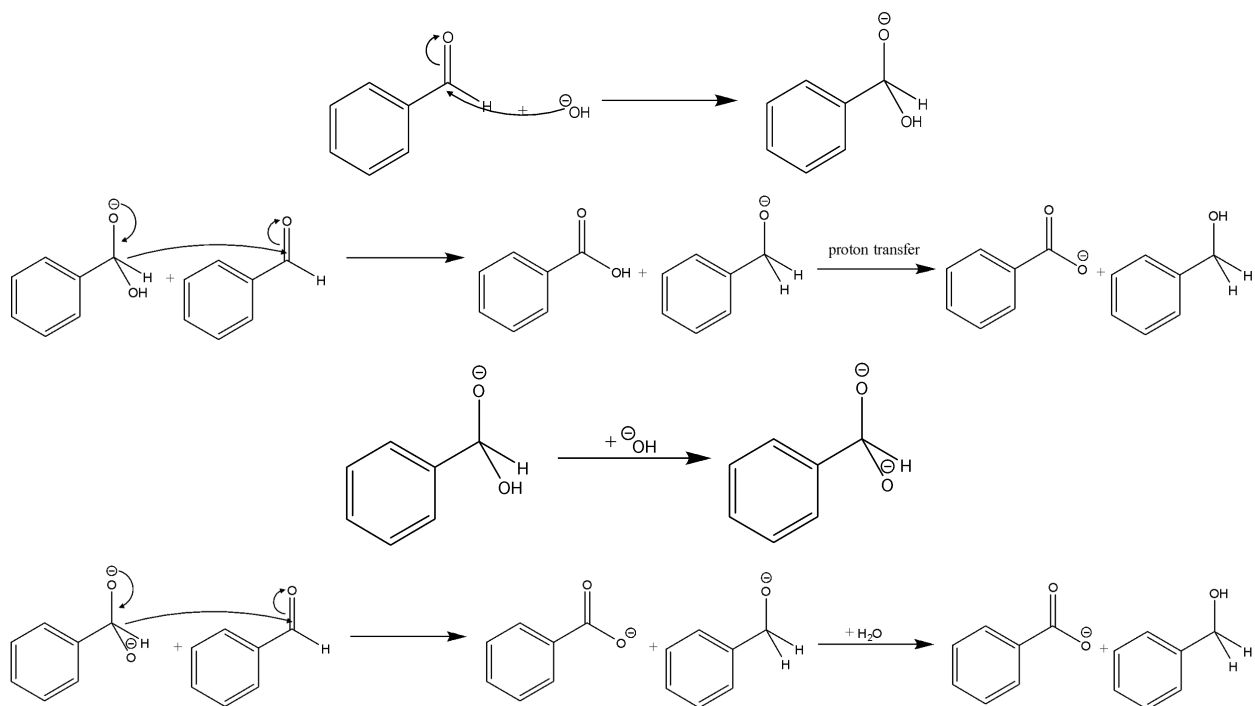
At low concentrations of base, the aldehyde undergoes nucleophilic addition with OH⁻ to form an alkoxide then reacts with another aldehyde to form the products. At high concentrations of base, the alkoxide is deprotonated by base first to from a doubly charged anion before reacting with aldehyde to form the products.

We can derive the following simplified rate equation:

$$rate = k_1[RCHO]^2[OH^-] + k_2[RCHO]^2[OH^-]^2$$

An experiment was conducted with constant concentrations of aldehyde but varying concentrations of base. The results of the experiment are given below.

$[OH^-]$ / M	0.10	0.20	0.30	0.40	0.80
Initial rate / M s^{-1}	1.24×10^{-6}	4.33×10^{-6}	9.26×10^{-6}	1.60×10^{-5}	6.16×10^{-5}

Determine the ratio k_2/k_1.

Leave your answer to the nearest integer.

Solution:

30

There are multiple ways to solve this question. Let us begin by simplifying the rate equation.

$$rate = k_1'[OH^-] + k_2'[OH^-]^2$$

Where $k_1' = k_1[RCHO]^2$ and $k_2' = k_2[RCHO]^2$.

We can convert this equation into a linear form and run a linear regression using a tool like a graphing calculator or Desmos.

$$\frac{rate}{[OH^-]} = k_1' + k_2'[OH^-]$$

[OH⁻] / M	0.10	0.20	0.30	0.40	0.80
Initial rate / M s⁻¹	1.27×10^{-6}	4.44×10^{-6}	9.51×10^{-6}	1.65×10^{-5}	6.34×10^{-5}
$\frac{rate}{[OH^-]}$	1.27×10^{-5}	2.22×10^{-5}	3.17×10^{-5}	4.125×10^{-5}	7.925×10^{-5}

The graph we get is:

x_1		y_1
.1		$1.27 \cdot \frac{10^{-6}}{.1}$
.2		$4.44 \cdot \frac{10^{-6}}{.2}$
.3		$9.51 \cdot \frac{10^{-6}}{.3}$
.4		$1.65 \cdot \frac{10^{-5}}{.4}$
.8		$6.34 \cdot \frac{10^{-5}}{.8}$
------		------

$y_1 \sim ax_1 + b$

STATISTICS   RESIDUALS

$r^2 = 1$ e_1 [plot]

$r = 1$

PARAMETERS

$a = 0.0000950822$

$b = 0.00000319041$
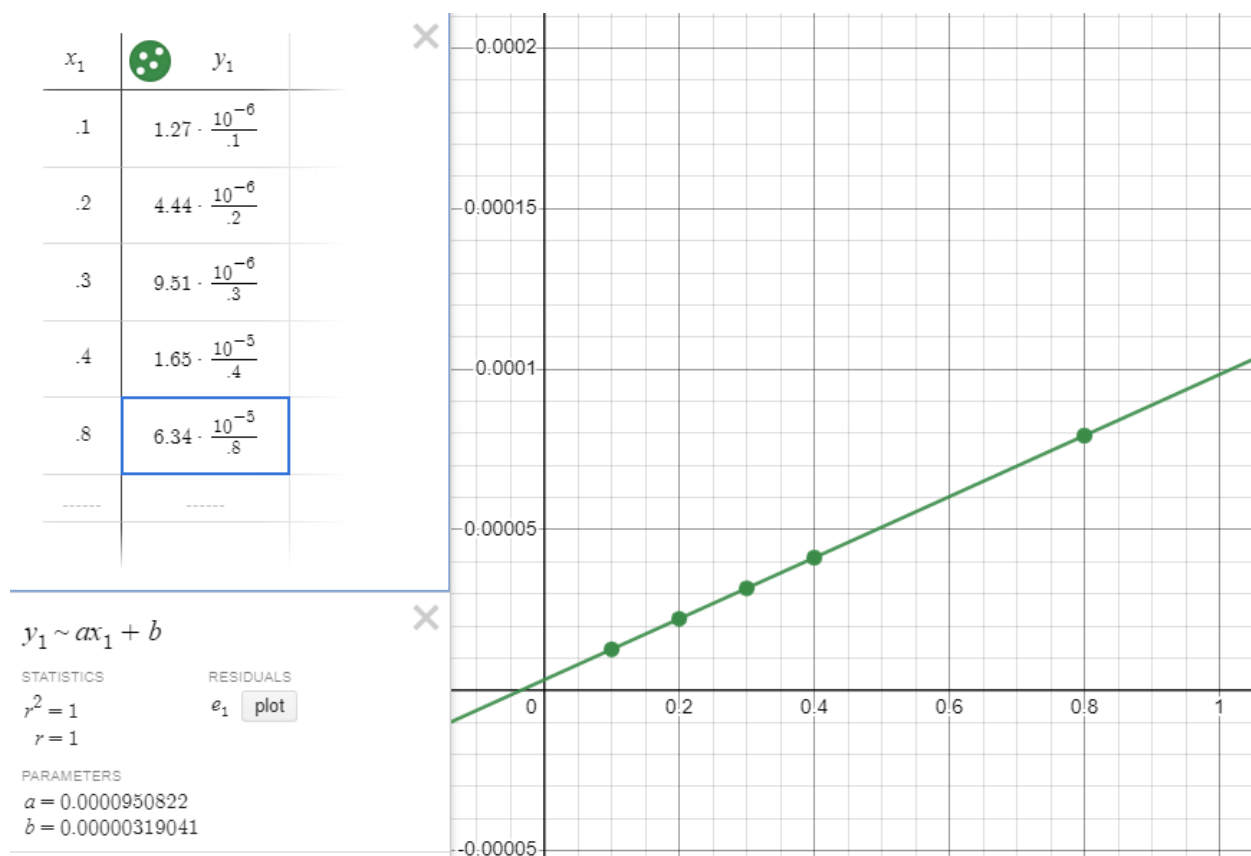
We get $k_2' = 9.50822 \times 10^{-5}$ and $k_1' = 3.19041 \times 10^{-6}$. Also, the value of r = 0.9999998054, which means we have got the right relationship.

Finally, the ratio $k_2/k_1 = k_2'/k_1' = $ **29.8 = 30**

AR55: Liberté, Radicalé, Substituté

Timmy was conducting a fun experiment on a hydrocarbon (see figure that follows).

Figure 1: At last! The elixir of life!

The hydrocarbon in question is 2-methylbutane. Timmy added chlorine gas to it under the presence of ultraviolet light. The ratio of rate of substitution for primary and secondary hydrogens is 1:3.

Give the structure of the monosubstituted isomer which forms in the greatest proportion. (Only molecules which are completely identical are to be classified as the same isomer.)

Include stereochemistry where relevant.

Solution:
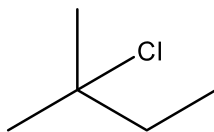
2-methylbutane has this structure:

2-methylbutane
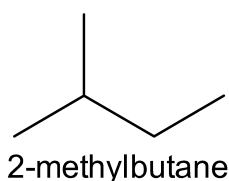
The following isomers are possible (note that stereoisomers are also different)

A1   A2   B1   B2

C   D
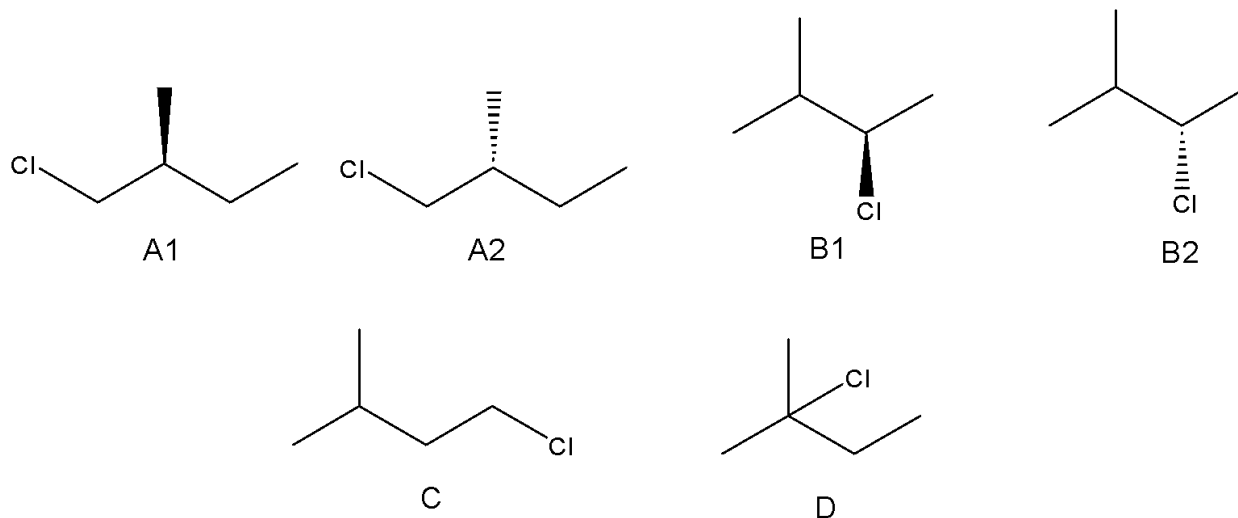
Each isomer's formation proportion depends on the number of hydrogens and the rate of each hydrogen's substitution.

Isomer	Number of hydrogens	Type of hydrogen
A	6	Primary
A1 & A2	3 each	Primary
B	2	Secondary
B1 & B2	1 each	Secondary
C	3	Primary
D	1	Tertiary

We can eliminate B1 and B2, since 1 secondary is going to be lower than 1 tertiary. We then need to compare 3 primary and 1 tertiary. Since a secondary hydrogen is substituted 3 times as fast as a primary hydrogen, and a tertiary hydrogen is substituted even faster, we can deduce that D will be the product formed in the greatest proportion.

AR56: The Devil in the Dark

All hands on deck! You and the crew of your starship have received a distress call from an obscure mining colony on the planet Berzelius. Upon arriving there, you learn that the miners working there have been frequently attacked in recent months by a mysterious creature that lives in the colony's deepest, darkest mines. To make matters worse, your on-board Science Officer, LTA Spork, encountered an accident in one of the mines while researching the creature and is currently unconscious.

Luckily, LTA Spork left behind the following star-log notes on a vital molecule, called "Molecule **Y**" that builds the very cells of this alien life-form, and may be key to defeating it:

(1) Molecule **Y** has a molar mass of 161 g mol^{-1} (3 s.f.).
(2) Molecule **Y** contains 2 silicon atoms.
(3) Molecule **Y** can also be produced in a reaction between trimethylchlorosilane and Gas **X** under alkaline conditions.
(4) Molecule **Y** has a refractive index of 1.4090.
(5) Gas **X** is a pungent-smelling gas that turns moist red litmus paper blue.

To better understand this mysterious creature, you must present the CAS number of Molecule **Y** to the Berzilian Scientific Authority (ignoring the dashes in the number) for further analysis. With every second that passes, the risk of another attack increases! Good luck Captain! The future of Berzelius depends on you!

Give your answer in the form of the CAS Registry Number, omitting any dashes. You may find this database helpful: https://commonchemistry.cas.org/ (note that this database cannot search by formula, so you need to key in the full name).

Solution:

999973

Molecule **Y** is hexamethyldisilazane.

Gas **X** is ammonia, since it is a pungent gas that turns moist red litmus paper blue.

The reaction between trimethylchlorosilane and ammonia under alkaline conditions is similar to the alkylation of ammonia, except this time it's silylation:
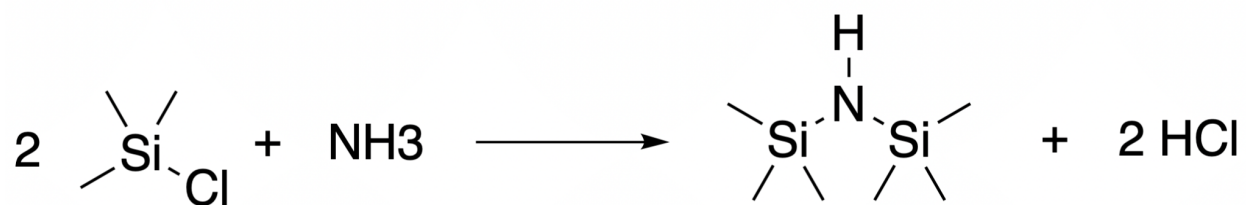
While more strictly an equilibrium reaction, in the actual reaction, HCl is constantly being neutralised by the alkaline medium. Thus, the product is produced in greater quantities. The reaction stops after each ammonia molecule has undergone alkylation twice since Molecule **Y** has only 2 silicon atoms.

Red herrings like the molar mass and refractive index can be used to verify that the product above is Molecules **Y**. Hence, Molecule **Y** is hexamethyldisilazane with a CAS number of **999973.**

AR57: Ammonolysis

Ammonolysis is the process of splitting NH_3 into NH_2^- and H^+. Similarly to water, liquid ammonia also undergoes auto-ionisation, $2NH_3 \rightleftharpoons NH_2^- + NH_4^+$.

Consider the first and second pKas of NH_4^+.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad\qquad pK_{a,1} = 9.27$$
$$NH_3 \rightleftharpoons NH_2^- + H^+ \qquad\qquad pK_{a,2} = 37.0$$
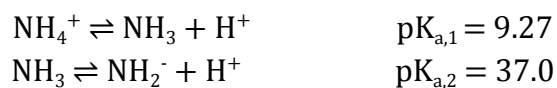
It is given that the rate of the forward reaction of the auto-ionisation of liquid ammonia is k_1 = 1.9×10^{-38}. Let the rate of the reverse reaction of the auto-ionisation of liquid ammonia be k_{-1}.

Find the value of $\log_{10}(k_{-1})$.

Leave your answer to 4 significant figures.

Solution:

-9.991

We can write the equilibrium constant of the reaction as $K = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2}$.

We also notice that $\frac{K_{a,2}}{K_{a,1}} = \frac{[NH_2^-][H^+]}{[NH_3]} \cdot \frac{[NH_4^+]}{[NH_3][H^+]} = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2} = K$.

Hence, we can compute the value of $K = \frac{10^{-37.0}}{10^{-9.27}} = 10^{-27.73}$.

We know that $K = \frac{k_1}{k_{-1}} \Rightarrow k_{-1} = \frac{k_1}{K} = \frac{1.9 \times 10^{-38}}{10^{-27.73}}$.

Therefore, we can compute the answer as $\lg(k_{-1}) = \lg\left(\frac{1.9 \times 10^{-38}}{10^{-27.73}}\right) = -\mathbf{9.991}$ (4 s.f.).

AR58: A failed synthesis

A student executed the following synthesis. He discovered that in both steps, monosubstitution occurred, and concluded that sterics were a major factor in controlling the product of the reaction.
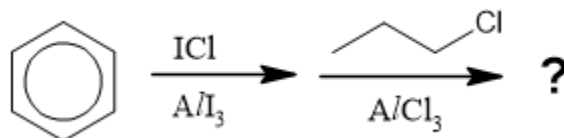
What is the major product formed?

Leave your answer as an organic structure.

Solution:
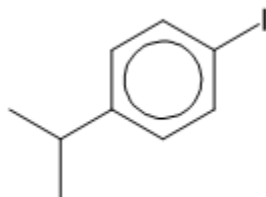
Sterics play the larger role in the second step, indicating that the para product was probably formed due to the large iodine substituent.

In the first step, the iodobenzene is formed because iodine is less electronegative and I^+ is formed as the electrophile.

In the second step, the carbocation formed undergoes a rearrangement to give the more stable tertiary carbocation. It is then substituted at the para position due to steric hindrance.

The intermediates are shown below:
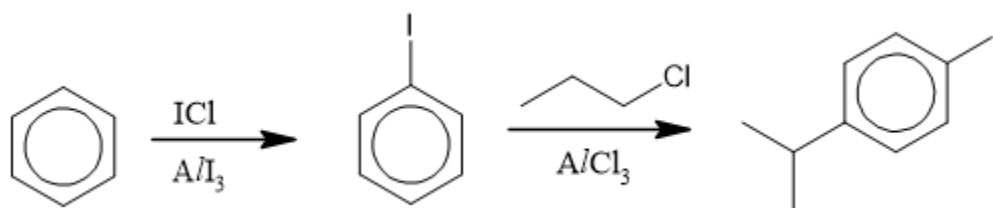
AR59: Nascent and Reactive

Nucleophilic substitution reactions are typically taught to proceed by two mechanisms: the S_N2 and S_N1 mechanism. Under both these mechanisms, benzene is unlikely to undergo nucleophilic substitution. However, experimentally, it is observed that benzene can undergo nucleophilic substitution under certain conditions. This mechanism is termed nucleophilic aromatic substitution (NAS) or S_NAr. An example of the mechanism is shown below.
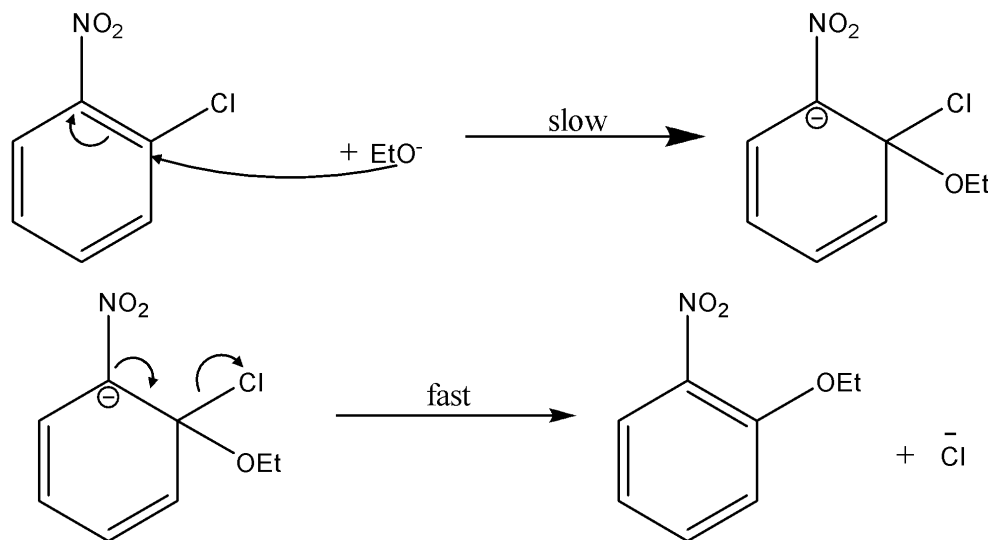
In the slow step, the nucleophile attacks the benzene ring, destroying the aromaticity and generating a carbanion intermediate with the ring negatively charged. In the fast step, the leaving group takes the negative charge and leaves, regenerating the aromaticity.

Different aromatic compounds may undergo NAS at different rates - in general, the rate of substitution increases when reaction intermediates are more stable. Consider the following compounds:

| 1 | 2 | 3 | 4 |
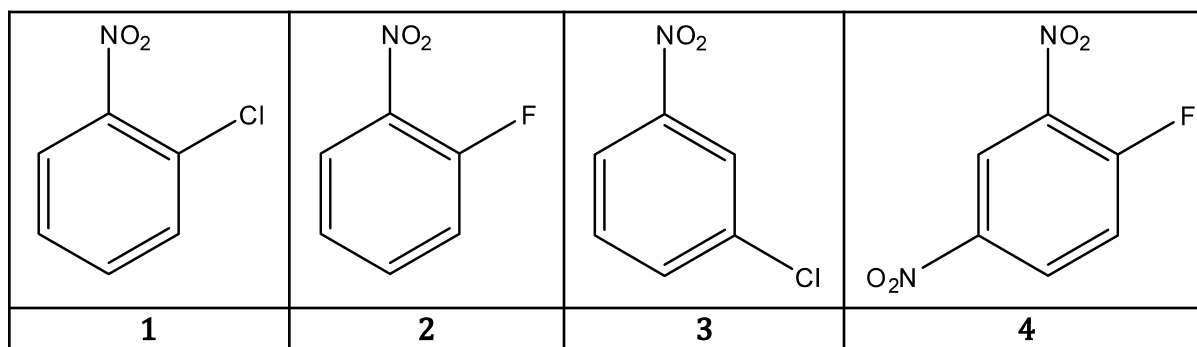
Arrange the above compounds in ascending order of their relative rates of nucleophilic substitution with the same arbitrary nucleophile.

(Hint: The trends may or may not be the same as that of S_N1 or S_N2. Consider which step(s) determine the rate of substitution.)

Leave your answer as a 4-digit number.

Solution:

3124

The first key thing to realise is that the rate determining step is not the C-X bond cleavage step, but rather the initial attack of the nucleophile. Hence, the leaving group's influence is not in its bond strength as you may have expected, but rather in activating the benzene ring to attack by the nucleophile.

Since Cl is less electronegative than F, the chlorobenzenes have a lower partial positive charge on the benzene ring and hence the benzene ring is less attractive to nucleophiles. Hence, **2 > 1**.

Between the chlorobenzenes, the *ortho* isomer is likely to be faster than the *meta* isomer. This is because in the *ortho* isomer, the negative charge in the intermediate can delocalise into the electron withdrawing nitro group, stabilising it and making its formation more feasible. This can be seen in the resonance structures below:
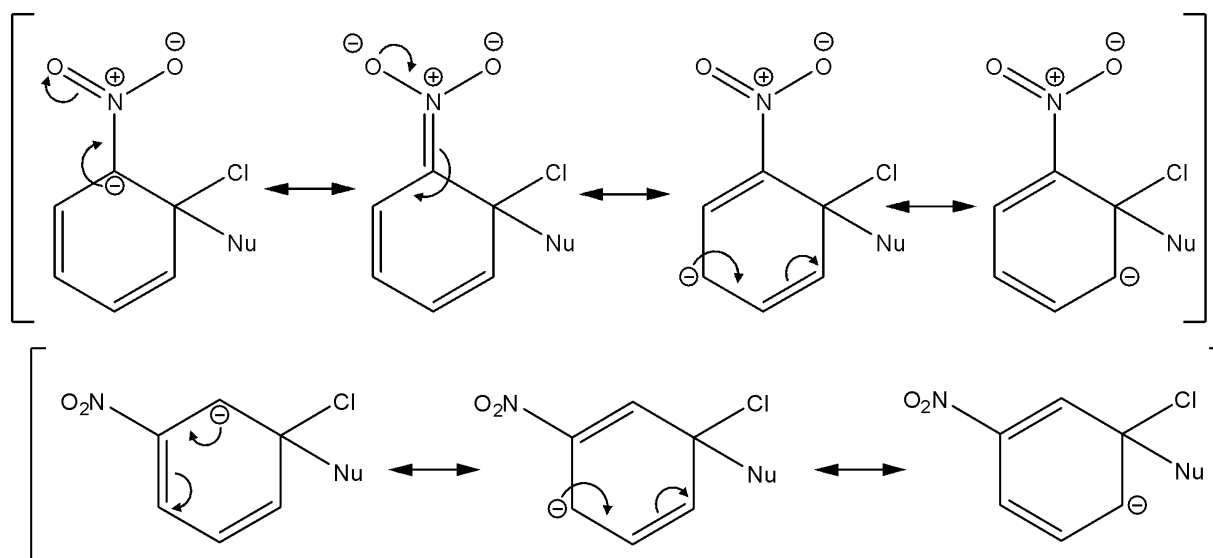
Hence, we deduce that **1 > 3.**

Lastly, between **2** and **4**, **4** has two rather than one electron withdrawing groups so the intermediates are more stabilised and form more readily. **4 > 2**.

Hence, **3 < 1 < 2 < 4**, so the answer to key in is **3124**.

AR60: G, small k, big K

Despite being commonly taught as separate topics, the concepts in energetics, kinetics and equilibria can be strikingly interconnected.

To illustrate this, we present 3 equations which relate variables such as the Gibbs free energy change (ΔG), rate constant (k) and equilibrium constant (K) of any reversible reaction,

$$\Delta G = -\ RT \ln K \ \text{-----} \ (1)$$

$$k = Ae^{-\frac{E_a}{RT}} \ \text{-----} \ (2)$$

$$K = \frac{k}{k'} \ \text{-----} \ (3)$$

where
- ΔG is the Gibbs free energy change (in Jmol^{-1}),
- k is the rate constant for the *forward* reaction,
- k' is the rate constant for the *backward* reaction,
- K is the equilibrium constant,
- R is the molar gas constant (in J mol^{-1} K^{-1}),
- T is the temperature (in K),
- A is the pre-exponential factor, which is an experimentally determined constant associated with the collision frequency of reactant particles. Assume it remains constant as temperature varies,
- E_a is the activation energy of the reaction (in J mol^{-1}).

From these equations, and using your own knowledge of energetics and equilibria, which of the following statement(s) is/are **true**?

1. At very high temperatures, $\Delta S \approx R \ln \frac{k}{k'}$.
2. For an exothermic reaction, when temperature is increased, the rate constant of the forward reaction, k, decreases.
3. For an endothermic reaction, the inequality $k < k'$ must be true.
4. For a reaction in which ΔG decreases as temperature increases, $A > A'$.
5. For a reaction spontaneous at all temperatures, $E_a > E_a'$.

If the statement is true, indicate T. If the statement is false, indicate F. Leave your answer as a concatenated string of characters. For example, if your answers are true, true, true, true, false, leave your answer as TTTTF.

Solution:

TFFTF

1. At very high temperatures, $\Delta S \approx R \ln \frac{k}{k'}$.

Substituting the expression for K from equation (3) into (1),

$$\Delta G = -RT \ln(\frac{k}{k'}) \text{ ----- (4)}$$

Substituting the expression for K from equation (2) into (4),

$$\Delta G = -RT \ln(\frac{Ae^{-\frac{E_a}{RT}}}{A'e^{-\frac{E_a'}{RT}}})$$

$$= -RT \ln(\frac{A}{A'}e^{\frac{E_a'-E_a}{RT}})$$

$$= -RT \ln(\frac{A}{A'}) - RT \ln(e^{\frac{E_a'-E_a}{RT}})$$

$$= -RT \ln(\frac{A}{A'}) - RT(\frac{E_a'-E_a}{RT})$$

$$= -RT \ln(\frac{A}{A'}) - (E_a' - E_a)$$

Note that the difference in activation energies of the forward and reverse processes is the enthalpy change (ΔH) of the reaction. This relationship can be seen by drawing an energy profile diagram.

Since $\Delta H = E_a - E_a'$,

$$\Rightarrow \Delta G = -RT \ln(\frac{A}{A'}) + \Delta H \text{ ----- (5)}$$

We also know that $\Delta G = \Delta H - T\Delta S$. Comparing it with equation (5),

$$\Rightarrow \Delta S = R \ln(\frac{A}{A'})$$

Recall that $k = Ae^{-\frac{E_a}{RT}}$. At very high values of T, the exponent term $-\frac{E_a}{RT}$ tends towards 0, and k tends towards A. At high temperatures, the equation can be re-expressed as

$$\Delta S \approx R \ln(\frac{k}{k'})$$

and therefore this relation is **true**.

2. For an exothermic reaction, when temperature is increased, the rate constant of the forward reaction, k, decreases.

From equation (2), we expect the magnitude of k to increase when T increases, regardless of the sign of the enthalpy change of the forward reaction. Intuitively, this is accurate, knowing that the rate of any reaction would increase as temperature increases. Hence this is **false**.

3. For an endothermic reaction, the inequality $k < k'$ must be true.

Note that the magnitude of A is different for the forward and reverse reactions, since different reactant particles are involved. Even though it is true that $E_a > E_a'$ for an endothermic reaction, if the magnitude of A and A' differs, it will not always be the case that $k < k'$ holds true for all reactions. Hence this is **false**.

4. For a reaction in which ΔG decreases as temperature increases, $A > A'$.

Recall equation (5) which we have derived earlier.
$$\Delta G = -RT \ln\left(\frac{A}{A'}\right) + \Delta H \text{ ----- (5)}$$
If ΔG for a reaction decreases as the temperature T increases, it indicates that the $-RT \ln\left(\frac{A}{A'}\right)$ term becomes more negative for more positive values of T. The term $\ln\left(\frac{A}{A'}\right)$ is positive, hence $A > A'$ is **true**.

5. For a reaction spontaneous at all temperatures, $E_a > E_a'$.

For a reaction spontaneous at all temperatures, $\Delta G < 0$ at all values of T. From the equation $\Delta G = \Delta H - T\Delta S$, this is true when $\Delta H < 0$ and $\Delta S > 0$ for the reaction.

Recall that $\Delta H = E_a - E_a'$. As $\Delta H < 0$, the reaction is exothermic, hence the correct expression is $E_a < E_a'$ and the statement is **false**.

AR61: What is this, a crossover episode?

Adenosine triphosphate (ATP) is the biological energy source used by our bodies. It has the structure shown below:
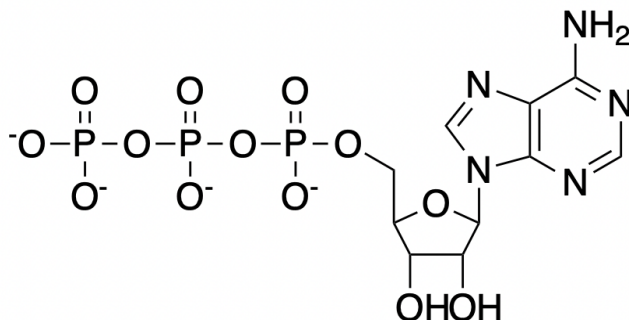
Several statements are made regarding ATP.

1. During oxidative phosphorylation, ADP is oxidised to ATP by the addition of one phosphate group.
2. The five-membered ribose ($(CH_2)_4O$) ring is planar.
3. If thymidine triphosphate were to be hydrolysed to thymidine diphosphate in the same process that ATP is hydrolysed to ADP, it would be expected to release the same amount of energy.
4. Energy is released during the conversion of ATP to ADP due to the breakage of the high-energy P−O bond.
5. As the lone pair on the $-NH_2$ group is delocalised into the aryl system of the adenosine component, it is expected to be less basic than usual.

If the statement is true, indicate T. If the statement is false, indicate F. Leave your answer as a concatenated string of characters. For example, if your answers are true, true, true, true, false, leave your answer as TTTTF.

Leave your answer as a string of five characters, in capital letters.

Solution:

FFTFT

1. During oxidative phosphorylation, ADP is oxidised to ATP by the addition of one phosphate group.

False, While a phosphate group is indeed added, ATP and ADP have the same oxidation states. A condensation reaction has occurred, analogous to formation of an ester from an alcohol and carboxylic acid, which does not change oxidation states.

2. The five-membered tetrahydrofuran ($(CH_2)_4O$) ring is planar.

False, 5-membered rings usually have an envelope shape where one atom is bent out of the plane, and the tetrahydrofuran moiety is no exception.

3. If thymidine triphosphate were to be hydrolysed to thymidine diphosphate in the same process that ATP is hydrolysed to ADP, it would be expected to release the same amount of energy.

True, the only difference between thymidine triphosphate and ATP is that the base attached at the 1-position is a thymine instead of adenine. The enthalpy change is not affected as the bonds broken and formed are the same.

4. Energy is released during the conversion of ATP to ADP due to the breakage of the high-energy P−O bond.

False, while a common misconception in biology, bond-breaking is *always* endothermic. The energy released comes from subsequent steps where energy released from bond-forming is greater than the initial investment of energy needed to hydrolyse the P-O bond.

5. As the lone pair on the $-NH_2$ group is delocalised into the aryl system of the adenosine component, it is expected to be less basic than usual.

True, this is analogous to how phenols and anilines (aminobenzene) are rendered less basic by the delocalisation of the lone pair into the benzene ring.

AR62: Oreganic Chemistry

Oregano contains many organic compounds. One such compound is rosmarinic acid, and its structure is shown below.
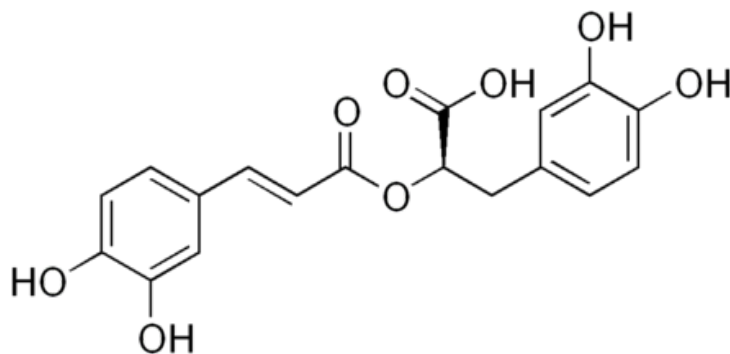
Structure of rosmarinic acid

A sample of rosmarinic acid was heated in an open test tube for a prolonged period with acidified $KMnO_4$, with vigorous stirring. How many **distinct organic products** are formed at the end of the reaction, assuming the reaction goes to completion?

Leave your answer as an integer.

Solution:

1

We can see that $KMnO_4$ will cleave the alkene, yielding the red and blue products below. Under prolonged heating in acidic conditions, the ester hydrolyses to yield ethanedioic acid, which undergoes further oxidation to give CO_2 gas.

$KMnO_4$ also does side-chain oxidation on the purple phenyl ring, yielding the purple structure, which is **identical to the red structure**, and the remainder of the green structure is oxidised to ethanedioic acid, which also undergoes further oxidation to give CO_2 gas.

Hence, only one unique product (the red / purple product) is formed.