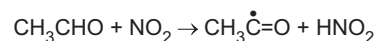


- 2 Ethanal, CH_3CHO , reacts with nitrogen dioxide, NO_2 . The products of the first step of this reaction are a $\text{CH}_3\dot{\text{C}}=\text{O}$ radical and a molecule of nitrous acid, HNO_2 .



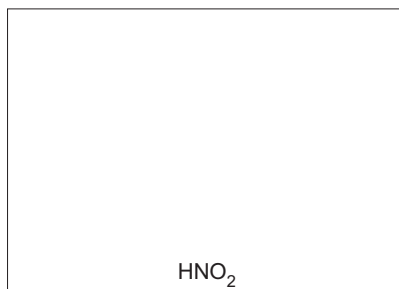
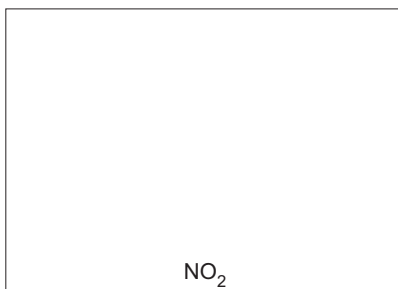
- (a) (i) Use **two** words to complete the sentence.

This reaction involves of the single covalent bond between a hydrogen atom and a carbon atom in CH_3CHO .

[1]

- (ii) The hydrogen atom mentioned in (a)(i) forms a covalent bond with one of the oxygen atoms of an NO_2 molecule. An NO_2 molecule has a single, unpaired electron on the nitrogen atom. All electrons are paired in an HNO_2 molecule.

Draw dot-and-cross diagrams of NO_2 and HNO_2 in the boxes. Show outer shell electrons only.



[1]

- (iii) Use VSEPR theory to predict the bond angle at the nitrogen atom in an HNO_2 molecule.

bond angle = [1]

- (b) The rate equation for the reaction between CH_3CHO and NO_2 is shown.

$$\text{rate} = k[\text{CH}_3\text{CHO}][\text{NO}_2]$$

Under certain conditions, when the concentrations of both CH_3CHO and NO_2 are $0.200 \text{ mol dm}^{-3}$, the rate of the reaction is $1.53 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Calculate the value of the rate constant, k , under these conditions. Give the units of k .

$k = \dots\dots\dots$ units [2]

- (c) The reaction mixture described in (b) is monitored over a period of time.

Predict whether the graph of $[\text{NO}_2]$ against time shows a constant half-life.

Explain your answer.

prediction

explanation

[1]

- (d) NO_2 also reacts with ozone, O_3 .

The rate equation is shown.

$$\text{rate} = k_1[\text{NO}_2]$$

Under certain conditions, the value of k_1 is 0.0848 s^{-1} .

The reaction has a constant half-life under these conditions.

Calculate the half-life in seconds.

half-life = s [1]

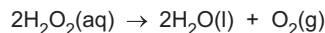
- (e) NO_2 is present in the exhaust gases of cars. It can react with carbon monoxide, CO , on the surface of a heterogeneous catalyst in the car's catalytic converter.

Describe the mode of action of this heterogeneous catalyst.

.....
.....
.....
.....
.....
.....
..... [2]

[Total: 9]

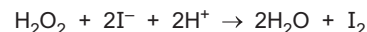
- 3 (a) Solid manganese(IV) oxide, MnO_2 , catalyses the decomposition of hydrogen peroxide.



State the type of catalysis for this reaction. Explain your answer.

.....
..... [1]

- (b) Hydrogen peroxide reacts with iodide ions in acidic conditions as shown.



The initial rate of this reaction is investigated with different concentrations of H_2O_2 , I^- and H^+ . The results obtained are shown in Table 3.1.

Table 3.1

experiment	$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	$[\text{I}^-]/\text{mol dm}^{-3}$	$[\text{H}^+]/\text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.0450	0.0300	0.0125	2.42×10^{-3}
2	0.0225	0.0600	0.0125	2.42×10^{-3}
3	0.0225	0.120	0.0125	4.84×10^{-3}
4	0.0450	0.120	0.0500	9.68×10^{-3}

- (i) Use the information in Table 3.1 to deduce the rate equation for this reaction.

Explain your reasoning.

.....
.....
.....
.....
.....
.....
.....
..... [4]

- (ii) Use your rate equation from (b)(i) and the data from Experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

$k = \frac{1}{3} \dots \dots \dots$ units $\dots \dots \dots$ [2]

- (c) The rate of the thermal decomposition of azomethane, $\text{CH}_3\text{N}=\text{NCH}_3$, is investigated.

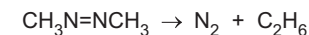


Fig. 3.1 shows the results obtained. The reaction is first order with respect to $\text{CH}_3\text{N}=\text{NCH}_3$.

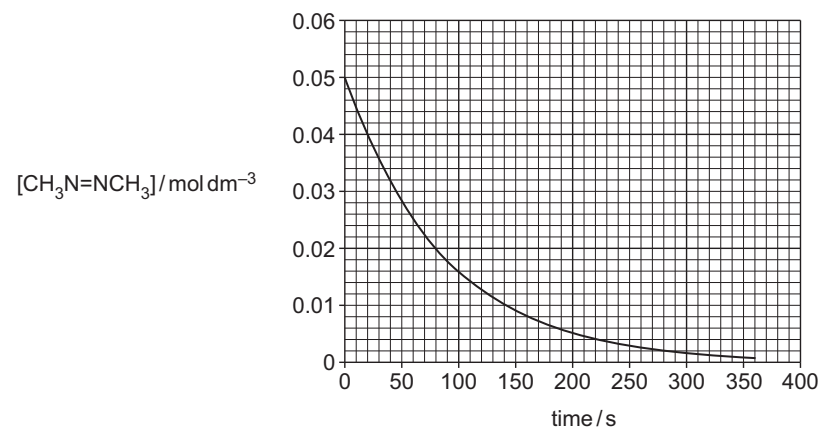


Fig. 3.1

- (i) Use Fig. 3.1 to calculate **two** half-lives, $t_{1/2}$, to show that the reaction is first order.

.....
.....
.....
..... [2]

- (ii) Use your answer to (c)(i) to calculate the rate constant, k , for the decomposition of azomethane.

$k = \dots \dots \dots \text{s}^{-1}$ [1]

- (d) Describe the effect of increasing temperature on the rate constant and on the rate of a reaction.

.....
.....
..... [1]

[Total: 11]

4 (a) Nitrogen monoxide, NO, reacts with hydrogen, as shown in reaction 3.



(i) The rate equation for reaction 3 is shown.

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

Complete Table 4.1.

Table 4.1

the order of reaction with respect to $[\text{H}_2]$	
the order of reaction with respect to $[\text{NO}]$	
the overall order of the reaction	

[1]

(ii) Predict how the initial rate for reaction 3 changes when the concentration of NO is halved.

..... [1]

(iii) Predict how the initial rate for reaction 3 changes when the concentrations of NO and H_2 are both increased **three** times.

..... [1]

(iv) Suggest why reaction 3 is unlikely to proceed by a mechanism involving only a single step.

.....

..... [1]

(v) Suggest equations for the **three** steps of the reaction mechanism for reaction 3.

Each step involves a reaction between **two** molecules.

step 1 $\rightarrow$

step 2 + $\rightarrow \text{N}_2\text{O} +$

step 3 $\text{N}_2\text{O} +$ $\rightarrow$ +

[2]

(vi) Suggest the role of N_2O in this mechanism.

Explain your reasoning.

.....

..... [1]

(b) Iodine, I_2 , reacts with thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, as shown in reaction 4.



Reaction 4 is carried out in the presence of a large excess of I_2 . Under these conditions, the reaction is first order with respect to $[\text{S}_2\text{O}_3^{2-}]$ and zero order with respect to $[\text{I}_2]$.

The half-life, $t_{1/2}$, for reaction 4 is 720 s under certain conditions.

Calculate the value of the rate constant, k , for reaction 4. Include the units of k .

$k =$ units [1]

(c) The reaction between iodide ions, $\text{I}^-(\text{aq})$, and peroxydisulfate ions, $\text{S}_2\text{O}_8^{2-}(\text{aq})$, is catalysed by $\text{Co}^{3+}(\text{aq})$. The mechanism is similar to the mechanism of this reaction when $\text{Fe}^{3+}(\text{aq})$ is used as the catalyst.

(i) State the type of catalysis that occurs in this reaction.

Explain your reasoning.

.....

..... [1]

(ii) Write **two** equations to show how $\text{Co}^{3+}(\text{aq})$ catalyses this reaction.

equation 1

equation 2 [2]

(iii) Suggest why this reaction is slow in the absence of $\text{Co}^{3+}(\text{aq})$.

.....

..... [1]

[Total: 12]