

## Mark schemes

1

- (a) Order wrt **D** = 1 OR first OR [D] OR [D]<sup>1</sup>

*Ignore working*

1

Order wrt **E** = 2 OR second OR [E]<sup>2</sup>

1

- (b) (At time zero/start) the concentrations are known

1

- (c) M1 (Calculate) gradient (of tangent/curve/graph)  
*Allow description of gradient calculation:*

*Change in conc / time*

1

M2 at t=0 or at start of graph/curve

*M2 scored only if M1 gained*

*Ignore the word initial*

1

[5]

2

- (a) Iodine is not involved in (or before) the rate determining / slow(est) / limiting step (in the mechanism)

*Ignore, iodine does not appear in the rate equation or iodine concentration does not affect the rate*

1

- (b)  $k = \left( \frac{8.64 \times 10^{-7}}{(5.82 \times 10^{-2}) \times (4.76 \times 10^{-1})} \right) = 3.1(2) \times 10^{-5}$

*Mark for answer*

1

mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>

*Mark units separately, i.e. only these units but can be in any order*

1

- (c) Rate =  $k [H^+]$

*If wrong or missing CE = 0*

1

(Large excess of propanone) so [CH<sub>3</sub>COCH<sub>3</sub>] is (effectively) constant

1

[5]

3

- (a) Consider experiments 1 and 2: [B constant]

[A] increases × 3: rate increases by 3<sup>2</sup> therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases  $\times 2$ : rate should increase  $\times 2^2$  but only increases  $\times 2$

Therefore, halving [B] halves rate and so 1st order with respect to B

Rate equation: rate =  $k[A]^2[B]$

(b) rate =  $k[C]^2[D]$  therefore  $k = \text{rate} / [C]^2[D]$

$$k = \frac{7.2 \times 10^{-4}}{(1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2})} = 57.0$$

*Allow consequential marking on incorrect transcription*

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

*Any order*

(c) rate =  $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} (\text{mol dm}^{-3} \text{s}^{-1})$

**OR**

Their  $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

(d) Reaction occurs when molecules have  $E \geq E_a$

Doubling T by 10 °C causes many more molecules to have this  $E$

Whereas doubling [E] only doubles the number with this  $E$

(e)  $E_a = RT(\ln A - \ln k) / 1000$

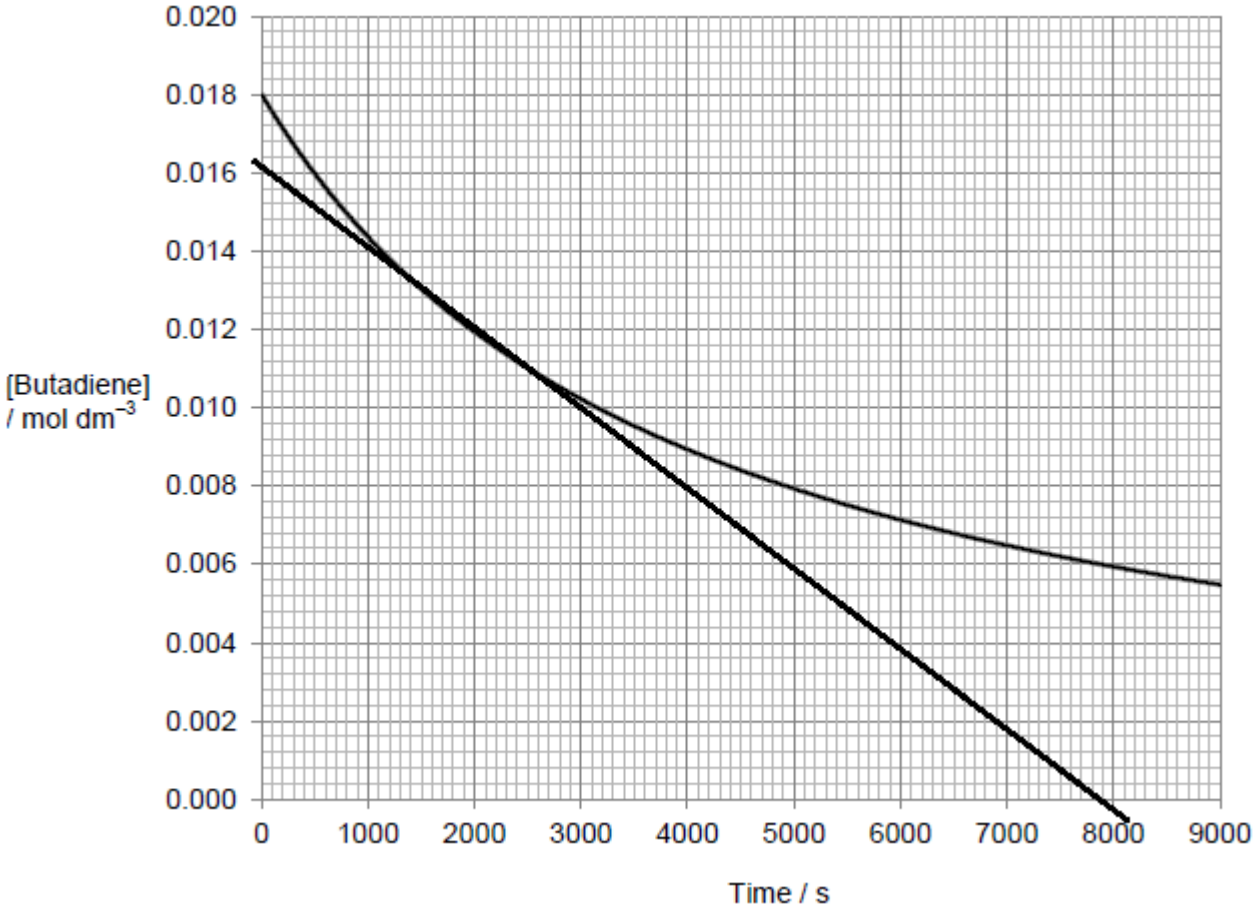
*Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ*

$$E_a = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 (\text{kJ mol}^{-1})$$

[12]

4

(a) Gradient drawn on graph



Line must touch the curve at 0.012 but must not cross the curve.

1

(b) Stage 1: Rate of reaction when concentration = 0.0120 mol dm<sup>-3</sup>

From the tangent

Change in [butadiene] = -0.0160 - 0 and change in time = 7800 - 0

*Extended response*

1

Gradient = -(0.0160 - 0) / (7800 - 0) = -2.05 × 10<sup>-6</sup>

Rate = 2.05 × 10<sup>-6</sup> (mol dm<sup>-3</sup> s<sup>-1</sup>)

1

Stage 2: Comparison of rates and concentrations

Initial rate / rate at 0.0120 = (4.57 × 10<sup>-6</sup>) / (2.05 × 10<sup>-6</sup>) = 2.23

*Marking points in stage 2 can be in either order*

1

Initial concentration / concentration at point where tangent drawn = 0.018 / 0.012 =

1.5

1

Stage 3: Deduction of order

If order is 2, rate should increase by factor of  $(1.5)^2 = 2.25$  this is approximately equal to 2.23 therefore order is 2nd with respect to butadiene

1  
[6]

5 B

[1]

6

(a)  $k = \text{rate} / [\text{A}]^2$  or  $\frac{3.3 \times 10^{-5}}{(4.2 \times 10^{-3})^2}$

1

= 1.87 or 1.9

*Answer scores 2*

*1.90 scores first mark only (incorrect rounding)*

1

$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

*Any order and independent of calculation*

1

(b) Expt 2 rate =  $1.167 \times 10^{-4} - 1.2 \times 10^{-4}$  ( $\text{mol dm}^{-3} \text{s}^{-1}$ )

*If answers in table are not those given here, check their value of k in part (a) or use of alternative k.*

1

Expt 3 [A] =  $9.7 \times 10^{-3} - 9.8(1) \times 10^{-3}$  ( $\text{mol dm}^{-3}$ )

*If their k is incorrect in part (a) mark this part consequentially e.g. if  $k = 7.9 \times 10^{-3}$  due to lack of squaring in (a)*

Using alternative value for k

*expt 2  $4.9 \times 10^{-7}$*

Expt 2 rate =  $1.4(4) \times 10^{-4}$  ( $\text{mol dm}^{-3} \text{s}^{-1}$ )

*expt 3  $1.5 \times 10^{-1}$*

Expt 3 [A] =  $8.85 \times 10^{-3}$  ( $\text{mol dm}^{-3}$ )

*(expt 2  $6.24 \times 10^{-5} \times \text{their } k$ )*

*(expt 3  $0.0134 / \sqrt{k}$ )*

1

(c) Slow step or rds involves only A

**OR**

B does not appear in the slow step or the rds

**OR**

B only appears after the slow step or the rds

*Not B has no effect on the rate or B is not in the rate equation*

*Allow "it" for B*

1

[6]

7

(a) (i) 2

1

(ii) 0

1

(b) (i) 
$$K = \frac{6.64 \times 10^{-5}}{(4.55 \times 10^{-2}) \times (1.70 \times 10^{-2})^2}$$

*Correct answer for k with or without working scores 2.*

*First mark is for insertion of numbers into a correctly rearranged rate equ, k = etc.*

1

= 5.05 (range allowed 5.03–5.07)

*AE (-1) for copying numbers wrongly or swapping two numbers.*

1

mol<sup>-2</sup> dm<sup>+6</sup> s<sup>-1</sup>

*Mark units separately, ie only these units but can be in any order.*

1

(ii)  $8.3 \times 10^{-6}$  (mol dm<sup>-3</sup> s<sup>-1</sup>)

*Allow  $0.83 \times 10^{-5}$ .*

*Ignore units.*

**OR** if not  $8.3 \times 10^{-6}$ , look at their k in part(i) and if not 5.05

Allow ecf for their (incorrect)  $k \times (1.64 \times 10^{-6})$

1

[6]

8

(a) (i) 2 or two or second or [E]<sup>2</sup>

1

(ii) 1 or one or first or [F]<sup>1</sup> or [F]

1

(b) (i)  $k = \frac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$   
*mark is for insertion of numbers into a correctly rearranged rate equation, k = etc.*  
*AE (-1) for copying numbers wrongly or swapping two numbers.*

1

= 22.9 (Allow 22.9 – 24 after correct rounding)

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

*Any order.*

1

(ii)  $6.8(2) \times 10^{-3} \text{ (mol dm}^{-3} \text{s}^{-1}\text{)}$   
**OR** if their k is wrong, award the mark consequentially  
 a quick check can be achieved by using  
their answer =  $2.9768 \times 10^{-4}$  Allow  $2.9 - 3.1 \times 10^{-4}$  for the mark  
 their k

*Allow  $6.8 \times 10^{-3}$  to  $6.9 \times 10^{-3}$*

*Ignore units.*

1

[6]

9

(a) (i)  $k = \frac{8.4 \times 10^{-5}}{(4.2 \times 10^{-2})^2 \times 2.6 \times 10^{-2}}$  **OR**  $\frac{8.4 \times 10^{-5}}{(1.76 \times 10^{-3}) \times 2.6 \times 10^{-2}}$

*Mark is for insertion of numbers into a correctly rearranged rate equation, k = etc.*

*If upside down, score only units mark from their k*

*AE (-1) for copying numbers wrongly or swapping two numbers*

1

= 1.8(3)

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

*Any order*

*If k calculation wrong, allow units consequential to their k = expression*

1

(ii)  $5.67 \times 10^{-4} \text{ (mol dm}^{-3} \text{s}^{-1}\text{)}$  **OR** their k  $\times 3.1 \times 10^{-4}$

*Allow  $5.57 \times 10^{-4}$  to  $5.7 \times 10^{-4}$*

1

(b) (i) 2 or second or  $[D]^2$

1

(ii) 0 or zero or  $[E]^0$

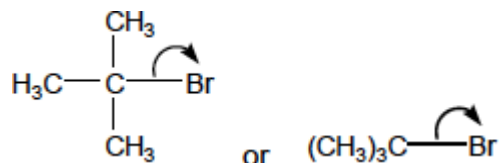
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(c) (i) Step 1 or equation as shown

*Penalise Step 2 but mark on*

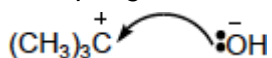
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(ii)



Ignore correct partial charges, penalise full / incorrect partial charges

*If Step 2 given above, can score the mark here for*



*allow:  $\text{OH}^-$  (must show lp)*

*If  $\text{S}_{\text{N}}2$  mechanism shown then no mark (penalise involvement of  $\text{:OH}^-$  in step 1)*

*Ignore anything after correct step 1*

1

[8]

10

(a) Exp 2  $4.5 \times 10^{-4}$

*Min 2sf*

1

Exp 3  $4.5 \times 10^{-3}$

*If three wrong answers, check their value of k in (b).*

1

Exp 4 0.043 OR  $4.3 \times 10^{-2}$  OR 0.044 OR  $4.4 \times 10^{-2}$

*They can score all 3 if they have used their (incorrect) value of k. see below.*

$$\text{Exp 2 rate} = k \times (1.0125 \times 10^{-4})$$

$$\text{Exp 3 [Q]} = 0.02/k$$

$$\text{Exp 4 [P]} = 0.0913/k$$

1

(b)  $k = \frac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$

*Mark is for insertion of numbers into a correctly rearranged rate equation, k = etc*

*If upside down, score only units mark from their k*

*AE (-1) for copying numbers wrongly or swapping two numbers*

1

= 4.4(4) (allow 40/9)

1

$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

*Any order*

*If k calculation wrong, allow units consequent to their k expression*

1

[6]