$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(l) + 3\,H_2O(l)$$

In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial $[Br^-]$ (mol L^{-1})	Initial $[BrO_3^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Rate of Disappearance of BrO_3^- (mol L^{-1} s^{-1})
1	0.00100	0.00500	0.100	2.50×10^{-4}
2	0.00200	0.00500	0.100	5.00×10^{-4}
3	0.00100	0.00750	0.100	3.75×10^{-4}
4	0.00100	0.01500	0.200	3.00×10^{-3}

(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br^-

(ii) BrO_3^-

(iii) H^+

(b) Write the rate law for the overall reaction.

(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

Answer:

(a) (i) 1st order with respect to Br^-; in experiments 1 and 2, a doubling of the $[Br^-]$ results in the doubling of the initial rate, and indication of 1st order

(ii) 1st order with respect to BrO_3^-

using expt. 1 & 3

$rate_1 = k[Br^-]^1[BrO_3^-]^m[H^+]^n$

$$\frac{rate_1}{[BrO_3^-]^m} = k[Br^-]^1[H^+]^n$$

$rate_3 = k[Br^-]^1[BrO_3^-]^m[H^+]^n$

$$\frac{rate_3}{[BrO_3^-]^m} = k[Br^-]^1[H^+]^n$$

$$\frac{rate_1}{[BrO_3^-]^m} = \frac{rate_3}{[BrO_3^-]^m}$$

$$\frac{0.000250}{(0.0050)^m} = \frac{0.000375}{(0.0075)^m}$$

$m = 1$

(iii) 2nd order with respect to H^+

using expt. 3 & 4

$rate_3 = k[Br^-]^1[BrO_3^-]^1[H^+]^n$

$$\frac{\text{rate}_3}{[\text{BrO}_3^-]^1[\text{H}^+]^n} = k[\text{Br}^-]^1$$

$\text{rate}_4 = k[\text{Br}^-]^1[\text{BrO}_3^-]^1[\text{H}^+]^n$

$$\frac{\text{rate}_4}{[\text{BrO}_3^-]^1[\text{H}^+]^n} = k[\text{Br}^-]^1$$

$$\frac{\text{rate}_3}{[\text{BrO}_3^-]^1[\text{H}^+]^n} = \frac{\text{rate}_4}{[\text{BrO}_3^-]^1[\text{H}^+]^n}$$

$$\frac{0.000375}{(0.00750)(0.100)^n} = \frac{0.00300}{(0.0150)(0.200)^n}$$

$n = 2$

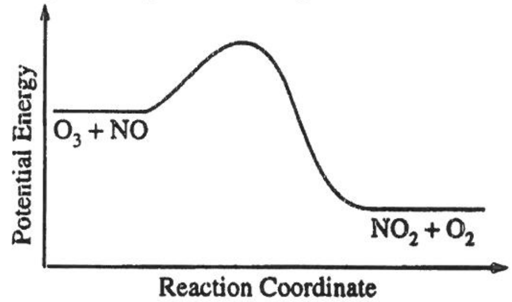
(b) $\text{rate} = k[\text{Br}^-]^1\,[\text{BrO}_3^-]^1\,[\text{H}^+]^2$

(c) $2.50\text{x}10^{-4} = k\,(0.00100)\,(0.00500)\,(0.100)^2$

$k = 5000\ \text{mol}^{-3}\text{L}^3\text{s}^{-1}$

Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction O_3 + NO → NO_2 + O_2. Clearly label the following directly on the diagram.

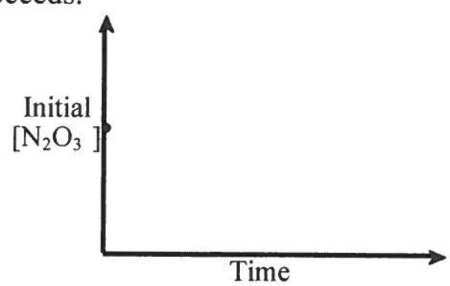


(i) The activation energy *(E_a)* for the forward reaction

(ii) The enthalpy change (ΔH) for the reaction

(b) The reaction 2 N_2O_5 → 4 NO_2 + O_2 is first order with respect to N_2O_5.

(i) Using the axes at right, complete the graph that represents the change in [N_2O_5] over time as the reaction proceeds.

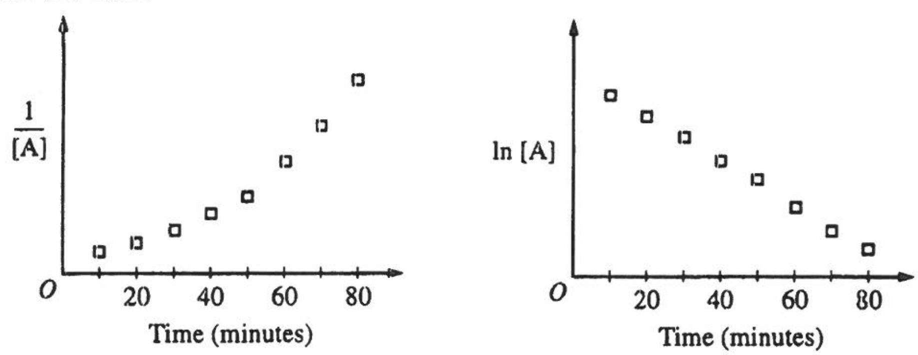


(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, *t*.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, *k*, could be determined.

(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, *k*? Explain.

(c) Data for the chemical reaction 2A → B + C were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.



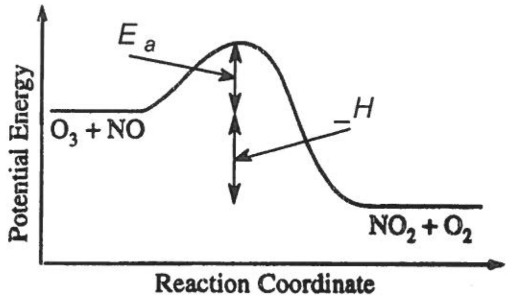
Use the information in the graphs above to answer the following.

(i) Write the rate-law expression for the reaction. Justify your answer.

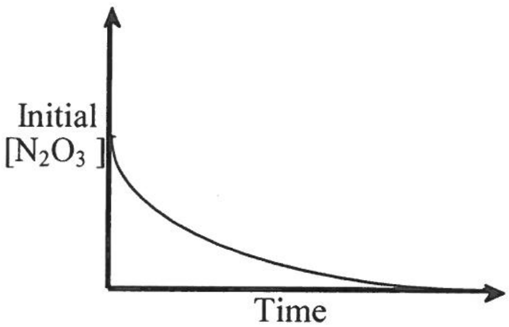
(ii) Describe how to determine the value of the rate constant for the reaction.

Answer

(a)



(b) (i)



(ii) the rate at time, *t*, is the slope of the tangent to the curve at time *t*

(iii) since the reaction is 1[st] order:

$\ln[N_2O_3]_t - \ln[N_2O_3]_o = -kt$

$$k = \frac{-\ln \frac{[N_2O_3]_t}{[N_2O_3]_o}}{t}$$

iv *k* would remain unchanged, it is temperature dependent, not concentration dependent.

(c)i since the graph of ln[A] is a straight line, this indicates that it its 1[st] order with respect to A, ∴, rate = k [A]

ii *k* = - slope of the straight line of the ln[A] *vs.* time graph