



AP Chemistry 1999 Sample Student Responses

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Knowing that the exponent for Br_2 is 1, we now can assess the order of NO by comparing 2 more experiments 2 & 3

$$\text{Ex 2} \quad 6.38 \times 10^{-4} = k [0.0160]^m [0.0240]$$

$$\text{Ex 3} \quad 6.42 \times 10^{-4} = k [0.0320]^m [0.0060]$$

$$(1 = .5^m \cdot 4) = (.5^m = 1/4) \quad m=2 \quad \therefore \text{the reaction is}$$

2nd order with respect to NO and the rate law is:

$$\text{c) i) rate} = k [\text{NO}]^2 [\text{Br}_2]$$

$$\text{ii) } 3.24 \times 10^{-4} \text{ mol/L}\cdot\text{s} = k \left[0.0160 \frac{\text{mol}}{\text{L}}\right]^2 \left[0.0120 \frac{\text{mol}}{\text{L}}\right]$$

$$k = 3.24 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$\left(0.0160 \frac{\text{mol}}{\text{L}}\right)^2 \left(0.0120 \frac{\text{mol}}{\text{L}}\right) \quad k = 105. \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$$

d) This is not consistent with the given experimental observation because the rate law can be calculated from the molecularity of the slow, rate determining step. The proposed mechanism's slow step is bimolecular while the rate law dictates that it should be termolecular.

a) $\frac{2 \text{ mol NOBr}}{1 \text{ mol Br}_2} \therefore \text{rate of disappearance Br}_2 = \frac{1}{2}(3.24 \times 10^{-4}) = 1.62 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

b) $\text{Rate} = k[\text{NO}]^x [\text{Br}_2]^y$

Exp. 1 $= 3.24 \times 10^{-4} = k[.0160]^x [.0120]^y$

Exp. 2 $= 6.38 \times 10^{-4} = k[.0160]^x [.0240]^y$

$.508 = .5^y$

$\log .508 = y \log .5$

$y = .977 \approx 1$

$$\text{Exp. 2} \quad 6.38 \times 10^{-4} = k [0.016]^x [0.024]^1$$

$$\text{Exp. 3} \quad 6.42 \times 10^{-4} = k [0.032]^x [0.006]^1$$

$$.994 = .5^x (4)$$

$$.248 = .5^x$$

$$\log .248 = x \log .5$$

$$x = 2.01 \approx 2$$

The order of reaction is 1 in $\text{Br}_2(g)$ and 2 in $\text{NO}(g)$

$$\text{c) (i) Rate} = k [\text{NO}]^2 [\text{Br}_2]^1$$

$$\text{(ii) } 3.24 \times 10^{-4} = k [0.016]^2 [0.012]^1 \quad (\text{Exp. 1})$$

$$k = 105.4$$

$$6.38 \times 10^{-4} = k [0.016]^2 [0.024]^1$$

$$k = 103.8$$

$$6.42 \times 10^{-4} = k [0.032]^2 [0.006]^1$$

$$k = 104.5$$

$$k = 105 \text{ M}^4 \text{ s}^{-1}$$

$$\text{Units for } k \quad \frac{\text{M/s}}{\text{M}^3} = \text{M}^4/\text{s} \text{ or } \text{M}^4 \text{ s}^{-1}$$

d) No, it is not. The slow step in a reaction mechanism is the rate-determining step. The coefficients in this step are usually the orders of reaction for their reactants. Since the coefficient of NO in the slow step is not 2, this mechanism is not consistent with the given experimental data.

(a) Rate of Appearance of $\text{NOBr} = 3.24 \times 10^{-4} \text{ mol/L}\cdot\text{sec}$

There are 2 NOBr formed for every 1 Br_2 molecule

lost therefore: $\text{Rate of Appearance of NOBr} =$

2

Rate of disappearance of Br_2

$$\frac{3.24 \times 10^{-4} \text{ mol/L}\cdot\text{sec}}{2} = \boxed{1.62 \times 10^{-4} \text{ mol/L}\cdot\text{sec}}$$

2

$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k(\text{conc NO})^a (\text{conc Br}_2)^b}{k(\text{conc NO})^a (\text{conc Br}_2)^b}$ $\frac{3.24 \times 10^{-4}}{6.38 \times 10^{-4}} = \frac{k(0.0160)^a (0.0120)^b}{k(0.0160)^a (0.0240)^b}$ $.5 = 1 \cdot 1 \cdot .5^b$ $b = 1$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">order of Br₂ = 1</div>	$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k(\text{conc NO})^a (\text{conc Br}_2)^b}{k(\text{conc NO})^a (\text{conc Br}_2)^b}$ $\frac{6.38 \times 10^{-4}}{6.42 \times 10^{-4}} = \frac{k(0.0160)^a (0.0240)^b}{k(0.0320)^a (0.0060)^b}$ $1 = 1 \cdot .5^{2a} \cdot 4$ $1 = 2^a \quad a = 0$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">order of NO = 0</div>
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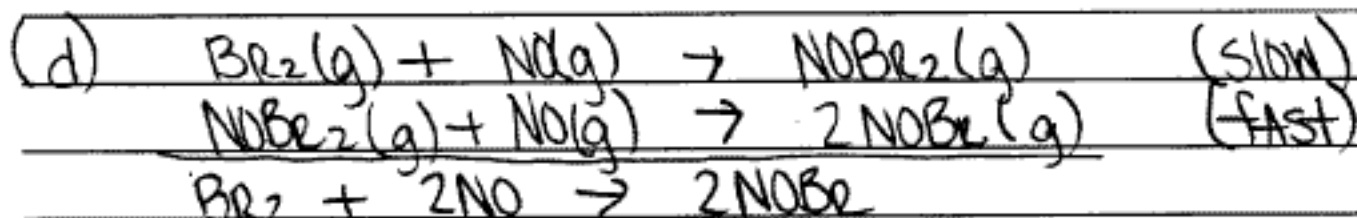
(c)

(i) $\text{Rate} = k(\text{conc Br}_2)$

(ii) $\text{Rate} = k(\text{conc Br}_2)$

$$k = \frac{\text{Rate}}{(\text{conc Br}_2)} = \frac{3.24 \times 10^{-4} \text{ mol/L} \cdot \text{sec}}{0.0120 \text{ mol/L}}$$

$k = .027 \text{ sec}^{-1}$



slow steps are rate determining and the slow step shown above is consistent with the rate law therefore the mechanism is correct.