AP Chemistry
1999 Sample Student Responses

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a) Using stoichemetric relations, we know that rate of dissapearance of Br_2 is twice the rate of appearance of NOBr ∴

$$3.24 \times 10^{-4}\ mol \cdot L^{-1} \cdot s^{-1}\ NOBr \left| \frac{1\ mol\ Br_2}{2\ mol\ NOBr} \right. = \boxed{1.62 \times 10^{-4}\ mol \cdot L^{-1} \cdot s^{-1}}$$

b) Rate constants can be determined by comparing 2 experiments when the molarity stays constant this is easy the equation is

$$\frac{rate\ 1}{rate\ 2} = \frac{k[NO]^m [Br_2]^n}{k[NO]^m [Br_2]^n} = \frac{3.24 \times 10^{-4}}{6.38 \times 10^{-4}} = \frac{k[.0160]^m [.0120]^n}{k[.0160]^m [.0240]^n}$$

$.5^n = .5$ ∴ $n = 1$ and the reaction is first-order with respect to Br_2

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

$$\text{Ex2}\quad 6.38\times10^{-4} = k\,[.0160]^m\,[.0240]^1$$
$$\text{Ex3}\quad 6.42\times10^{-4} = k\,[.0320]^m\,[.006]^1$$

$(1 = .5^m \cdot 4) = (.5^m = 1/4)$ $m=2$ ∴ the reaction is 2nd order with respect to NO and the rate law is:

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

ii) $3.24\times10^{-4}\ \text{mol/L}\cdot\text{s} = k\,[.0160\ \frac{\text{mol}}{\text{L}}]^2\,[.0120\ \frac{\text{mol}}{\text{L}}]$

$$k = \frac{3.24\times10^{-4}\ \frac{\text{mol}}{\text{L}\cdot\text{sec}}}{(.0160\ \frac{\text{mol}}{\text{L}})^2(.0120\ \frac{\text{mol}}{\text{L}})}$$

$$\boxed{k = 105.\ \frac{L^2}{\text{mol}^2\cdot s}}$$

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) $\frac{2 \text{ mol NOBr}}{1 \text{ mol } Br_2}$ ∴ rate of disappearance $Br_2 = \frac{1}{2}(3.24 \times 10^{-4}) =$ 1.62

1.62×10^{-4} mol $L^{-1} s^{-1}$

b) Rate $= k[NO]^x [Br_2]^y$

$$\frac{\text{Exp. 1}}{\text{Exp. 2}} = \frac{3.24 \times 10^{-4} = k[.0160]^x [.0120]^y}{6.38 \times 10^{-4} = k[.0160]^x [.0240]^y}$$

$.508 = .5^y$

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

$y = .977 \approx 1$

$$\frac{\text{Exp. 2} \quad 6.38 \times 10^{-4} = k[.016]^x [.024]^1}{\text{Exp. 3} \quad 6.42 \times 10^{-4} = k[.032]^x [.006]^1}$$

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

$.248 = .5^x$

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

$x = 2.01 \approx 2$

The order of reaction is 1 in $Br_{2(g)}$ and 2 in $NO_{(g)}$

c) (i) Rate $= k[NO]^2 [Br_2]^1$

(ii) $3.24 \times 10^{-4} = k[.016]^2 [.012]^1$ (Exp. 1)

$k = 105.4$

$6.38 \times 10^{-4} = k[.016]^2 [.024]^1$

$k = 103.8$

$6.42 \times 10^{-4} = k[.032]^2 [.006]^1$

$k = 104.5$

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

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

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 NOBr = 3.24×10^{-4} Mol/L·sec
There are 2 NOBr formed for every 1 Br_2 molecule lost therefore: $\frac{\text{Rate of appearance of NOBr}}{2}$ =

Rate of dissappearance of Br_2

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

(b) $\frac{\text{RATE}_1}{\text{RATE}_2} = \frac{k(\text{conc NO})^a(\text{conc Br}_2)^b}{k(\text{conc NO})^a(\text{conc Br}_2)^b}$

$\frac{3.24 \times 10^{-4}}{6.38 \times 10^{-4}} = \frac{k(.0160)^a(.0120)^b}{k(.0160)^a(.0240)^b}$

$.5 = 1 \cdot 1 \cdot .5^b$

$b = 1$

order of Br_2 = 1

$\frac{\text{RATE}_2}{\text{RATE}_3} = \frac{k(\text{conc NO})^a(\text{conc Br}_2)^b}{k(\text{conc NO})^a(\text{conc Br}_2)^b}$

$\frac{6.38 \times 10^{-4}}{6.42 \times 10^{-4}} = \frac{k(.0160)^a(.0240)^1}{k(.0320)^a(.0060)^1}$

$1 = 1 \cdot .5^a \cdot 4$

$1 = 2^a \quad a = 0$

order of NO = 0

(c)

(i) RATE = k (conc Br_2)

(ii) RATE = k (conc Br_2)

$k = \frac{\text{RATE}}{(\text{conc Br}_2)} = \frac{3.24 \times 10^{-4}\ \text{mol/L} \cdot \text{sec}}{.0120\ \text{mol/L}}$

k = .027 / sec

(d) $Br_2(g) + NO(g) \rightarrow NOBr_2(g)$ (slow)

$NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$ (fast)

$Br_2 + 2NO \rightarrow 2NOBr$

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