Section 6.6: Reaction Mechanisms

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1. (a) The elementary reaction $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ is of the form A + B → products, so the rate law equation for the reaction is
rate = $k[Ag^+(aq)][Cl^-(aq)]$

(b) The elementary reaction $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$ is of the form A + B → products, so the rate law equation for the reaction is
rate = $k[O_3(g)][NO(g)]$

(c) The elementary reaction $O_3(g) \rightarrow O_2(g) + O(g)$ is of the form A → products, so the rate law equation for the reaction is
rate = $k[O_3(g)]$

(d) The elementary reaction $O_3(g) + O(g) \rightarrow 2\ O_2(g)$ is of the form A + B → products, so the rate law equation for the reaction is
rate = $k[O_3(g)][O(g)]$

2. (a) Given: proposed mechanism for the reaction between iodine chloride gas and hydrogen gas:

$$ICl(g) + H_2(g) \rightarrow HI(g) + HCl(g) \quad \text{slow}$$
$$HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g) \quad \text{fast}$$

Required: the overall reaction
Solution:

$$\begin{array}{r} ICl(g) + H_2(g) \rightarrow HI(g) + HCl(g) \\ HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g) \\ \hline ICl(g) + H_2(g) + \cancel{HI(g)} + ICl(g) \rightarrow \cancel{HI(g)} + HCl(g) + HCl(g) + I_2(g) \end{array}$$

Overall reaction: $2\ ICl(g) + H_2(g) \rightarrow 2\ HCl(g) + I_2(g)$

(b) Given: experimentally determined rate law, rate = $k[ICl(g)]^2[H_2(g)]$
Required: whether the proposed mechanism agrees with the rate law equation
Solution: The proposed mechanism states that the first step is rate determining, so the overall reaction rate must be defined by the first step. The rate law equation for the first step is
$r = k[ICl(g)][H_2(g)] \neq k[ICl(g)]^2[H_2(g)]$.
Statement: The proposed mechanism does not agree with the experimentally determined rate law.

3. (a) Given: proposed mechanism for a reaction:

$$I_2(g) \rightarrow 2\ I(g) \quad \text{slow}$$
$$H_2(g) + 2\ I(g) \rightarrow 2\ HI(g) \quad \text{fast}$$

Required: the overall reaction
Solution:

$$\begin{array}{r} I_2(g) \rightarrow 2\ I(g) \\ H_2(g) + 2\ I(g) \rightarrow 2\ HI(g) \\ \hline I_2(g) + H_2(g) + \cancel{2\ I(g)} \rightarrow \cancel{2\ I(g)} + 2\ HI(g) \end{array}$$

Overall reaction: $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

(b) The reaction intermediate is I(g).

(c) The proposed mechanism states that the first step is rate determining, so the overall reaction rate must be defined by the first step. The rate law equation for the first step is $r = k[I_2(g)]$, so if the proposed mechanism is correct, the rate law equation is $r = k[I_2(g)]$.

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1. (a) An elementary step is a single chemical reaction of a series and involves a one-, two-, or three-entity collision that cannot be explained by simpler reactions.
(b) A reaction mechanism is a series of elementary steps that combine into a complete chemical reaction.
(c) A reaction intermediate is a chemical species that is both formed and consumed during a chemical reaction.
(d) The rate-determining step is the slowest elementary step of a reaction mechanism.
2. Answers may vary. Sample answer: Baking a cake is an analogy for a reaction with multiple steps. The reaction mechanism includes mixing liquid ingredients, mixing in dry ingredients, and baking. The rate-determining step is the baking step. The intermediate is carbon dioxide gas, which is formed when water is added to baking powder, one of the dry ingredients, and causes the cake to rise as the gas expands as the batter is heated.
3. It is unlikely that $2\ IF(g) + H_2(g) \rightarrow 2\ HF(g) + I_2(g)$ is a one-step reaction because the simultaneous collision of three entities is rare.
4. (a) The proposed mechanism is

$$O_3(g) \rightarrow O_2(g) + O(g) \quad \text{fast}$$
$$O_3(g) + O(g) \rightarrow 2\ O_2(g) \qquad \text{slow}$$

The proposed mechanism states that the second step is rate determining, so the overall reaction rate must be defined by the second step. The rate law equation for the second step is $r = k[O_3(g)][O(g)]$, so the rate law equation expected for this reaction mechanism is $r = k[O_3(g)][O(g)]$.
(b) Given: proposed mechanism in (a)
Required: the overall reaction
Solution:

$$O_3(g) \rightarrow O_2(g) + O(g)$$
$$\underline{O_3(g) + O(g) \rightarrow 2\ O_2(g)}$$
$$O_3(g) + O_3(g) + \cancel{O(g)} \rightarrow O_2(g) + \cancel{O(g)} + 2\ O_2(g)$$

Overall reaction: $2\ O_3(g) \rightarrow 3\ O_2(g)$
(c) The reaction intermediate is O(g).
5. (a) The proposed mechanism is

$$C_4H_9Br(aq) \rightarrow C_4H_9^+(aq) + Br^-(aq) \qquad \text{slow}$$
$$C_4H_9^+(aq) + H_2O(l) \rightarrow C_4H_9OH_2^+(aq) \qquad \text{fast}$$
$$C_4H_9OH_2^+(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + H_3O^+(aq) \quad \text{fast}$$

The proposed mechanism states that the first step is rate determining, so the overall reaction rate must be defined by the first step. The rate law equation for the first step is $r = k[C_4H_9Br(aq)]$, so the rate law equation expected for this reaction mechanism is $r = k[C_4H_9Br(aq)]$.
(b) Given: proposed mechanism in (a)

Required: the overall reaction
Solution:

$$C_4H_9Br(aq) \rightarrow C_4H_9^+(aq) + Br^{\square}(aq)$$
$$C_4H_9^+(aq) + H_2O(l) \rightarrow C_4H_9OH_2^+(aq)$$
$$C_4H_9OH_2^+(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + H_3O^+(aq)$$

$$C_4H_9Br(aq) + \cancel{C_4H_9^+(aq)} + H_2O(l) + \cancel{C_4H_9OH_2^+(aq)} + H_2O(l)$$
$$\rightarrow \cancel{C_4H_9^+(aq)} + Br^{\square}(aq) + \cancel{C_4H_9OH_2^+(aq)} + C_4H_9OH(aq) + H_3O^+(aq)$$

Overall reaction: $C_4H_9Br(aq) + 2\ H_2O(l) \rightarrow Br^{\square}(aq) + C_4H_9OH(aq) + H_3O^+(aq)$

(c) The intermediates in the proposed reaction mechanism are $C_4H_9^+(aq)$ and $C_4H_9OH_2^+(aq)$.

6. The two requirements that must be met for a reaction mechanism to be plausible are 1) the steps must sum to give the overall balanced equation for the reaction and 2) the reaction mechanism must agree with the experimentally determined rate law.

7. The friend's explanation is incorrect. A rate law cannot be determined directly from an overall because the equation does not identify the rate-determining step.

8. (a) Given: proposed reaction mechanism:

$$NO(g) + NO(g) \rightarrow N_2O_2(g)$$
$$N_2O_2(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Required: the overall reaction
Solution:

$$NO(g) + NO(g) \rightarrow N_2O_2(g)$$
$$N_2O_2(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

$$NO(g) + NO(g) + \cancel{N_2O_2(g)} + O_2(g) \rightarrow \cancel{N_2O_2(g)} + 2\ NO_2(g)$$

Overall reaction: $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

(b) The intermediate in the proposed reaction mechanism is $N_2O_2(g)$.

(c) The rate law equation for the first elementary reaction is $r = k[NO(g)]^2$, and the rate law equation for the second elementary reaction is $r = k[N_2O_2(g)][O_2(g)]$. Neither of these rate law equations matches the experimentally determined rate law equation, $r = k[NO(g)]^2[O_2(g)]$, so the reaction mechanism is not plausible and it is not possible to identify the rate-defining step.

9. (a) Given: proposed reaction mechanism:

$$NH_4^+(aq) \rightarrow NH_3(aq) + H^+(aq) \qquad \text{fast}$$
$$H^+(aq) + HNO_2(aq) \rightarrow H_2O(l) + NO^+(aq) \qquad \text{fast}$$
$$NH_3(aq) + NO^+(aq) \rightarrow NH_3NO^+(aq) \qquad \text{slow}$$
$$NH_3NO^+(aq) \rightarrow N_2(g) + H_2O(l) + H^+(aq) \qquad \text{fast}$$

Required: the overall reaction

Solution:

$$NH_4^+(aq) \rightarrow NH_3(aq) + H^+(aq)$$
$$H^+(aq) + HNO_2(aq) \rightarrow H_2O(l) + NO^+(aq)$$
$$NH_3(aq) + NO^+(aq) \rightarrow NH_3NO^+(aq)$$
$$NH_3NO^+(aq) \rightarrow N_2(g) + H_2O(l) + H^+(aq)$$

$$NH_4^+(aq) + \cancel{H^+(aq)} + HNO_2(aq) + \cancel{NH_3(aq)} + \cancel{NO^+(aq)} + \cancel{NH_3NO^+(aq)}$$
$$\rightarrow \cancel{NH_3(aq)} + \cancel{H^+(aq)} + H_2O(l) + \cancel{NO^+(aq)} + \cancel{NH_3NO^+(aq)} + N_2(g) + H_2O(l) + H^+(aq)$$

Overall reaction: $HNO_2(aq) + NH_4^+(aq) \rightarrow N_2(g) + 2\ H_2O(l) + H^+(aq)$

(b) The intermediates in the proposed reaction mechanism are $NH_3(aq)$, $NO^+(aq)$, and $NH_3NO^+(aq)$.

(c) Given: experimentally determined rate law, rate = $k[HNO_2(aq)][NH_4^+(g)]$
Required: plausibility of the proposed mechanism
Solution: The proposed mechanism states that the third step is rate determining, so the overall reaction rate must be defined by the third step. The rate law equation for the third step is rate = $k[NH^3(aq)][NO^+(aq)] \neq k[HNO_2(aq)][NH_4^+(g)]$.
Statement: The proposed mechanism is not plausible because it does not agree with the experimentally determined rate law.