14.6 Reaction Mechanisms and Catalysis

The Components of a Reaction Mechanism

Chemistry Interactive: Mechanism of The Reaction Between NO_2 and CO

Mechanism 1

Step 1. (slow, rate-determining step)

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Mechanism 2, Step 1

Step 1. (slow, rate-determining step)

$2\,NO_2(g) \longrightarrow NO_3(g) + NO(g)$

Why is the Initial Rate $\neq k[NO_2][CO]$?

BECAUSE experimentally it was found to be

$k[NO_2]^2$!

How to explain this ? ... Mechanisms.

Mechanism 2, Step 2

Step 2. (fast)

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

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Reaction Mechanisms – Rate Law – Catalyst -- Intermediate

$$NO_2(g) + CO(g) = NO(g) + CO_2(g)$$

There are two proposed mechanisms for this reaction

Mechanism 1

Step 1: $NO_2(g) + CO(g) = NO(g) + CO_2(g)$ *Slow step*

Mechanism 2 ✓

Step 1: $2\ NO_2(g) = NO_3(g) + NO(g)$ *Slow step*

Step 2: $NO_3(g) + CO(g) = NO_2(g) + CO_2(g)$ *Fast step*

Experimentally the rate law = $k[NO_2]^2$

a) Which mechanism best supports the experimentally determined rate law?

b) Intermediate – a) CO(g) b) $NO_3(g)$ c) NO(g) ✓ d) $CO_2(g)$ e) None

c) Catalyst – a) CO(g) b) $NO_3(g)$ c) NO(g) d) $CO_2(g)$ e) None ✓

a) MECHANISM 2: The sum of the steps = the balance chemical equation. Step 1 being the slow step would give an, $I.R. = k[NO_2]^2$, which matches the experimentally determine one.

b) INTERMEDIATE: Does not appear in balanced chemical equation. Appears as a Product in one step in the mechanism and subsequent gets used up as a Reactant in a subsequent step.

c) CATALYST : Does not appear in balanced chemical equation. Appears as a Reactant in one step in the mechanism and is then regenerated in a subsequent step.

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Reaction Mechanisms – Rate Law – Catalyst – Intermediate

$$Br_2(g) + H_2(g) = 2\ HBr(g)$$

Mechanism 2

Step 1:	$Br_2(g) \Leftrightarrow 2\ Br(g)$	*Fast in both directions*
Step 2:	$Br(g) + H_2(g) = HBr(g) + H(g)$	*Slow step* *
Step 3:	$H(g) + Br_2(g) = HBr(g) + Br(g)$	*Fast step*

a) Intermediate – **a)** Br(g) **b)** H(g) **c)** $H_2(g)$ ✓ **d)** HBr(g) **e)** None

b) Catalyst – **a)** Br(g) ✓ **b)** H(g) **c)** $H_2(g)$ **d)** HBr(g) **e)** None

The rate is determined by the slow step... Step 2.

Step 2: Initial Rate = $k[Br][H_2]$

↳ Intermediate. Usually short lived species, that can be difficult to isolate.

Better question, since I.R. is determined in lab with just $Br_2(g)$ & $H_2(g)$ to work with and with no prior expectation of an intermediate, what kind of Initial Rate might one expect to get experimentally?

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More Complex Mechanisms

$$2\,H_2(g) + 2\,NO(g) = N_2(g) + 2H_2O(g)$$

Mechanism:

Step 1: $2\,NO(g) \Leftrightarrow N_2O_2(g)$ *Fast in both directions*

Step 2: $N_2O_2(g) + H_2(g) = N_2O(g) + H_2O(g)$ *Slow step*

Step 3: $N_2O(g) + H_2(g) = N_2(g) + H_2O(g)$ *Fast step*

YES NO

What is the rate law for this reaction? Is there an intermediate? Is there a catalyst?

Slow step ... Step 2.

Initial Rate = $k_2[N_2O_2][H_2]$

↳ Intermediate

Step 1: Formation of N_2O_2, a fast equilibrium.

$Rate_f$: Rate of forward reaction.

$Rate_R$: Rate of reverse reaction.

@ Equilibrium, $Rate_f = Rate_R$

$Rate_f = k_f[NO]^2$

$Rate_R = k_R[N_2O_2]$

@ Eq. $k_R[N_2O_2] = k_f[NO]^2$

$[N_2O_2] = (k_f/k_R)[NO]^2$

Initial Rate = $k_2(k_f/k_R)[NO]^2[H_2]$

Initial Rate = $k[NO]^2[H_2]$

↳ $= k_2(k_f/k_R)$

these are all constants.