REACTION MECHANISMS

The rate law for the reaction is the **rate law for the rate-determining step** (slow step).

Use the experimental rate law to determine the validity of the following mechanisms by checking (1) that the elementary steps equal the reaction equation, (2) that the mechanism is probable, and (3) that the rate law determined from the mechanism is the same as the experimental rate law.

I. Reaction: $2\ NO_2Cl\ (g) \rightarrow 2\ NO_2\ (g) + Cl_2\ (g)$

Expt. Rate Law:
rate = k[NO_2Cl]

Mechanism 1
$2\ NO_2Cl \rightarrow 2\ NO_2 + Cl_2$

(1) mechanism steps = reaction √
(2) bimolecular mechanism √
(3) rate = k[NO_2Cl]^2 **NO**

Mechanism 2
$NO_2Cl \rightarrow NO_2 + Cl$ (slow)
$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ (fast)

$2\ NO_2Cl \rightarrow 2\ NO_2 + Cl_2$ {Cl cancels}

(1) mechanism steps = reaction √
(2) monomolecular mechanism √
(3) rate = k[NO_2Cl] √ **based on slow step**

Mechanism 2 appears to be valid.

II. Reaction: $2\ NO\ (g) + Br_2\ (g) \rightarrow 2\ NOBr\ (g)$

Expt. Rate Law:
rate = k[NO]^2[Br_2]

Mechanism 1
$2\ NO + Br_2 \rightarrow 2\ NOBr$

(1) mechanism steps = reaction √
(2) termolecular mechanism **NO rare**
(3) rate = k[NO]^2[Br_2] √

Mechanism 2
$NO + Br_2 \Leftrightarrow NOBr_2$ (fast, reversible)
$NOBr_2 + NO \rightarrow 2\ NOBr$ (slow)

$2\ NO + Br_2 \rightarrow 2\ NOBr$ {$NOBr_2$ cancels}

(1) mechanism steps = reaction √
(2) bimolecular mechanism √
(3) rate = k_2 [$NOBr_2$][NO] **NO based on slow slow step**

So neither Mechanism 1 nor Mechanism 2 appears to be valid.
BUT, in mechanism 2 the first elementary step attains equilibrium: rate forward = rate reverse.

rate forward = k_1 [NO][Br_2]   rate reverse = k_{-1} [$NOBr_2$]

k_1 [NO][Br_2] = k_{-1} [$NOBr_2$]   Rearrange and solve for [$NOBr_2$] .
[$NOBr_2$] = (k_1 / k_{-1}) [NO][Br_2]   Substitute into rate law.

rate = k_2 [$NOBr_2$][NO] = k_2 k_1 / k_{-1} [NO][Br_2] [NO]
rate = k [NO]^2 [Br_2]   where k = k_2k_1 / k_{-1} √

Mechanism 2 appears to be valid.