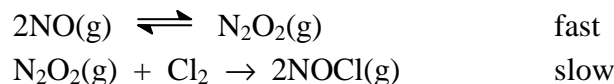


The mechanism for this reaction has been postulated to be that below.



Work out the rate law expected for this mechanism and hence show that it is consistent with the experimental rate law and the chemical equation.

Marks
4

The rate determining step is the slow, second step. As this is an elementary step, its rate law can be written down from its stoichiometry:

$$\text{rate} = k_2[\text{N}_2\text{O}_2(\text{g})][\text{Cl}_2(\text{g})]$$

where k_2 is the rate constant for this step.

This rate law involves the reactive intermediate N_2O_2 . The concentration of this cannot be controlled so this rate law cannot be experimentally tested.

The first reaction is a fast equilibrium. The rate laws for the forward and backward elementary reactions are:

$$\begin{array}{l} \text{rate of forward reaction} = k_1[\text{NO}(\text{g})]^2 \\ \text{rate of backward reaction} = k_{-1}[\text{N}_2\text{O}_2(\text{g})] \end{array}$$

where k_1 and k_{-1} are the rate constants for the forward and backward reactions, respectively.

At equilibrium, the rate of the forward and backward reactions are equal so

$$k_1[\text{NO}(\text{g})]^2 = k_{-1}[\text{N}_2\text{O}_2(\text{g})]$$

$$[\text{N}_2\text{O}_2(\text{g})] = \frac{k_1}{k_{-1}} [\text{NO}(\text{g})]^2 \quad \text{and} \quad \frac{[\text{N}_2\text{O}_2(\text{g})]}{[\text{NO}(\text{g})]^2} = \frac{k_1}{k_{-1}} = K_c$$

Substituting this value into the rate law for the second step gives,

$$\begin{aligned} \text{rate} &= k_2[\text{N}_2\text{O}_2(\text{g})][\text{Cl}_2(\text{g})] \\ &= k_2 \frac{k_1}{k_{-1}} [\text{NO}(\text{g})]^2 [\text{Cl}_2(\text{g})] = k' [\text{NO}(\text{g})]^2 [\text{Cl}_2(\text{g})] \quad \text{with } k' = k_2 \frac{k_1}{k_{-1}} = k_2 K_c \end{aligned}$$

This rate law is second order with respect to NO and first order with respect to Cl_2 , just as in the experimentally determined rate law in 2008-N-8. The proposed mechanism is thus consistent with the experiment.

ANSWER CONTINUES ON THE NEXT PAGE

The reaction is exothermic. Draw the potential energy vs reaction coordinate diagram for this mechanism, labelling all species that can be isolated.

The second step is the rate determining step so it has the larger activation energy. The reaction is exothermic so the products have lower enthalpy than the reactants.

