Marks 4

- The major pollutants emitted by cars, NO(g), CO(g), NO_2(g) and CO_2(g), can react according to the following equation.

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

The following rate data were collected at 215 °C.

Experiment	$[NO_2]_0$ (M)	$[CO]_0$ (M)	Initial rate (d$[NO_2]$/dt, M s^{-1})
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[NO_2]_0$ is kept constant and $[CO]_0$ is halved. There is no effect on the rate. The rate is not dependent on $[CO]_0$. It is zero order with respect to CO.

Between experiments (2) and (3), $[CO]_0$ is kept constant and $[NO]_0$ is doubled. This causes the rate to increase by a factor of (5.76×10^{-5} / 1.44×10^{-5}) = 4. The rate depends on the *square* of [NO]. It is second order with respect to NO.

Overall,

Rate = $k[NO_2]^2$

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

The rate law is determined by the rate of the slowest step. The concentration of the species in this step are determined only by steps before it.

As the rate does not depend on [CO], it must be involved in steps *after* the rate determining step.

The rate depends on $[NO_2]^2$ which is consistent with two molecules of NO_2 colliding in the rate determining step.

The simplest mechanism which fits these points and is consistent with the overall chemical reaction is:

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ **slow, rate determining step**

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ **fast**