2000 D Required

$O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_{2(g)}$

Consider the reaction represented above.

(a) Referring to the data in the table below, calculate the standard enthalpy change, for the reaction at 25°C. Be sure to show your work.

| | $O_{3(g)}$ | $NO_{(g)}$ | $NO_{2(g)}$ |
|---|---|---|---|
| Standard enthalpy of formation, $\Delta H_f^\circ$ at 25°C (kJ $mol^{-1}$) | 143 | 90. | 33 |

(b) Make a qualitative prediction about the magnitude of the standard entropy change, $\Delta S°$, for the reaction at 25°C. Justify your answer.

(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, for the reaction at 25°C. Explain your reasoning.

(d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

| Experiment Number | Initial $[O_3]$ (mol $L^{-1}$) | Initial [NO] (mol $L^{-1}$) | Initial Rate of Formation of $[NO_2]$ (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 1 | 0.0010 | 0.0010 | x |
| 2 | 0.0010 | 0.0020 | 2x |
| 3 | 0.0020 | 0.0010 | 2x |
| 4 | 0.0020 | 0.0020 | 4x |

(e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

Step I: $O_3 + NO \rightarrow O + NO_3$

Step II: $O + O_3 \rightarrow 2\ O_2$

Step III: $NO_3 + NO \rightarrow 2\ NO_2$