Application of Steady State Approximation

The mechanism of the reaction of $\text{H}_2$ with $\text{Br}_2$:

$$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$$

is not a concerted, 4-center transition state. The kinetics are, therefore, not first order in $\text{H}_2$ and first order in $\text{Br}_2$. Instead, there are five elementary reactions involved in the radical chain reaction:

\[
\begin{align*}
\text{Br}_2 & \rightarrow 2 \text{Br} & k_1 & \text{(Initiation)} \\
\text{Br} + \text{H}_2 & \rightarrow \text{HBr} + \text{H} & k_2 & \text{(Propagation)} \\
\text{H} + \text{Br}_2 & \rightarrow \text{HBr} + \text{Br} & k_3 & \text{(Propagation)} \\
\text{H} + \text{HBr} & \rightarrow \text{H}_2 + \text{Br} & k_4 & \text{(Termination)} \\
\text{Br} + \text{Br} & \rightarrow \text{Br}_2 & k_5 & \text{(Termination)}
\end{align*}
\]

Let’s write the expressions for the time rate of change of concentration of the radical species that do not appear in the balanced chemical reaction, as a preliminary step to applying the steady state approximation:

\[
\begin{align*}
\frac{d[\text{Br}]}{dt} &= 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 \\
\frac{d[\text{H}]}{dt} &= + k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \\
\frac{d[\text{Br}]}{dt} &= 2k_1[\text{Br}_2] - \frac{d[\text{H}]}{dt} - 2k_5[\text{Br}]^2 \text{ by subtraction}
\end{align*}
\]

Now, apply the steady state approximation: $\frac{d[\text{H}]}{dt} = 0 = \frac{d[\text{Br}]}{dt}$

\[
\begin{align*}
\frac{d[\text{Br}]}{dt} &= 0 = 2k_1[\text{Br}_2] - 0 - 2k_5[\text{Br}]^2 \\
[\text{Br}]_{ss} &= 2k_1[\text{Br}_2] / 2k_5 = k_1[\text{Br}_2] / k_5 = (k_1 / k_5)[\text{Br}_2] \\
[\text{Br}]_{ss} &= (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2}
\end{align*}
\]

\[
\begin{align*}
\frac{d[\text{H}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \\
k_2[\text{Br}][\text{H}_2] &= k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] = [\text{H}](k_3[\text{Br}_2] + k_4[\text{HBr}]) \\
[\text{H}]_{ss} &= k_2[\text{Br}][\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \text{ next, substitute in } [\text{Br}]_{ss} = (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2} \\
[\text{H}]_{ss} &= k_2 (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2}[\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}])
\end{align*}
\]

\[
\begin{align*}
\frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \\
&= k_2 (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] \\
&+ k_2 (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) [\text{Br}_2] \\
&- k_4 (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) [\text{HBr}] \\
&= k_2 (k_1 / k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] * \{ 1 + (k_3 [\text{Br}_2] - k_4[\text{HBr}]) / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \}
\end{align*}
\]
Let’s just focus on the terms between the braces for moment:
\[
\{ 1+ \frac{(k_3[Br_2] - k_4[HBr])}{(k_3[Br_2] + k_4[HBr])} \} \quad \text{(next, get to common denominator)}
\]
\[
= \{ \frac{k_3[Br_2] + k_4[HBr] + (k_3[Br_2] - k_4[HBr])}{(k_3[Br_2] + k_4[HBr])} \}
\]
\[
= \{ \frac{2(k_3[Br_2])}{(k_3[Br_2] + k_4[HBr])} \}
\]
\[
\text{after dividing top and bottom by } k_3
\]

Now, let’s put this back into our expression for \(d[HBr]/dt\)
\[
d[HBr]/dt = k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2] * \{2[Br_2]/([Br_2] + (k_4/k_3)[HBr])\}
\]
\[
= 2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2][Br_2]/([Br_2] + (k_4/k_3)[HBr])
\]
\[
= 2k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]/([Br_2] + (k_4/k_3)[HBr])
\]

define \(k = 2k_2(k_1/k_5)^{1/2}\) and \(k’ = (k_4/k_3)\) (\(k’\) is not a pseudo-1st order rate constant here)
\[
d[HBr]/dt = k[Br_2]^{3/2}[H_2]/([Br_2] + k’[HBr])\] just as in equation 25.4 on page 868.

P.S. I do not guarantee that all brackets, parentheses, and braces are properly placed!