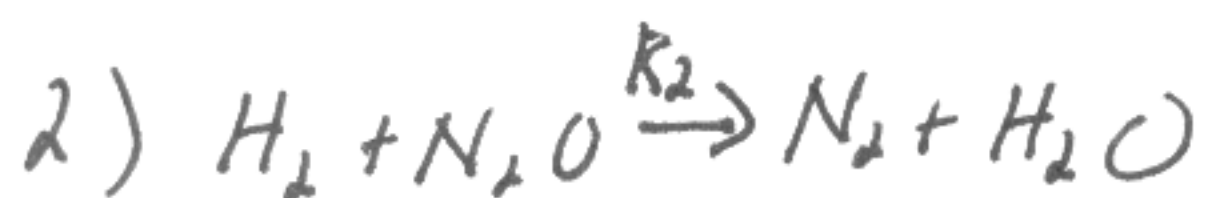
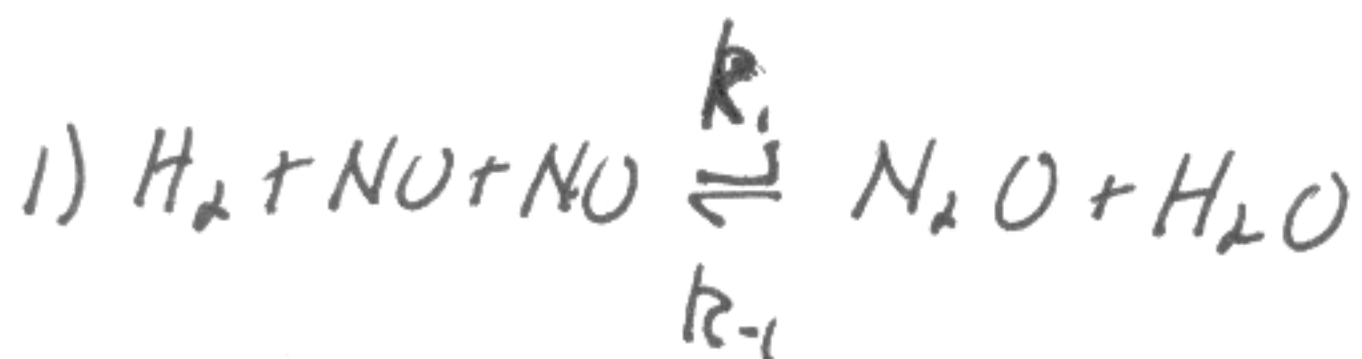


HW 14 Key

$$v(t) = k_{\text{obs}} [\text{H}_2] [\text{NO}]^2$$



$$\frac{d[\text{N}_2\text{O}]}{dt} = k_1 [\text{H}_2] [\text{NO}] [\text{NO}] - k_{-1} [\text{N}_2\text{O}] [\text{H}_2\text{O}] - k_2 [\text{H}_2] [\text{N}_2\text{O}]$$

$$\frac{d[\text{N}_2]}{dt} = k_2 [\text{H}_2] [\text{N}_2\text{O}]$$

assume SSA for N_2O : $0 = k_1 [\text{H}_2] [\text{NO}] [\text{NO}] - k_{-1} [\text{N}_2\text{O}] [\text{H}_2\text{O}] - k_2 [\text{H}_2] [\text{N}_2\text{O}]$

$$[\text{N}_2\text{O}] = \frac{k_1 [\text{H}_2] [\text{NO}]^2}{k_{-1} [\text{H}_2\text{O}] + k_2 [\text{H}_2]}$$

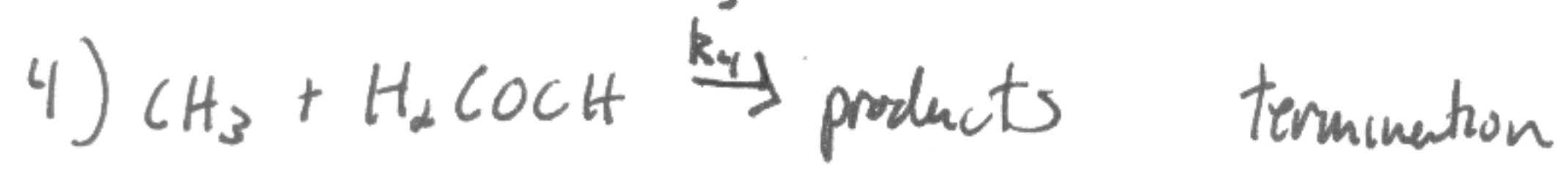
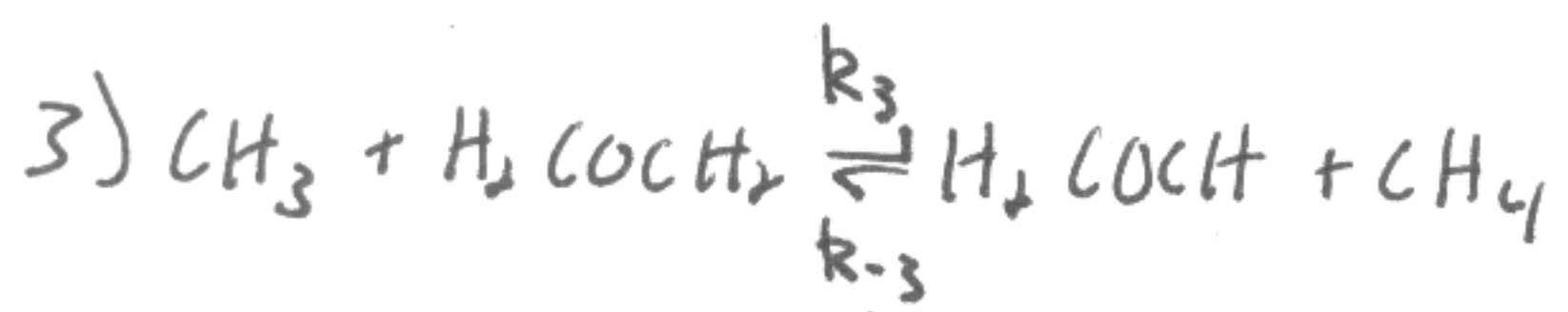
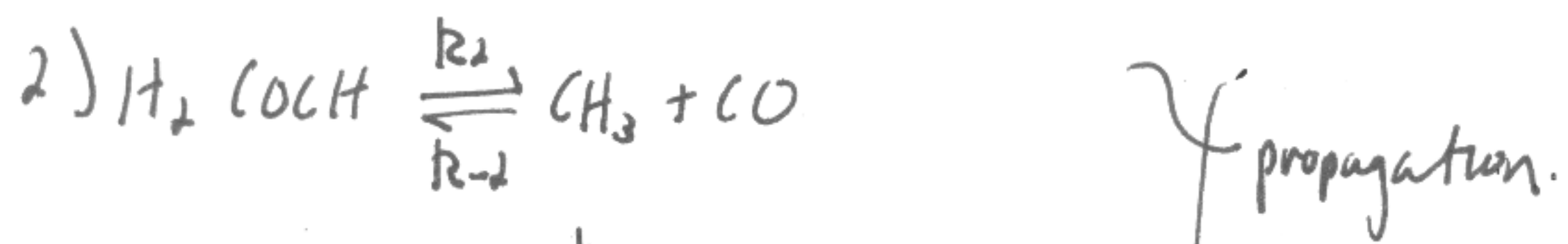
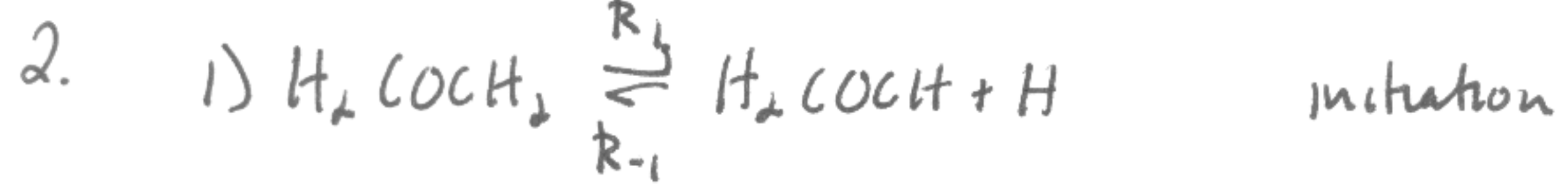
assume $k_2 \gg k_{-1} \Rightarrow [\text{N}_2\text{O}] = \frac{k_1 [\text{H}_2] [\text{NO}]^2}{k_2 [\text{H}_2]} = \frac{k_1}{k_2} [\text{NO}]^2$

plug into rate of product: $\frac{d[\text{N}_2]}{dt} = \cancel{k_2} [\text{H}_2] \left(\frac{k_1}{\cancel{k_2}} \right) [\text{NO}]^2$

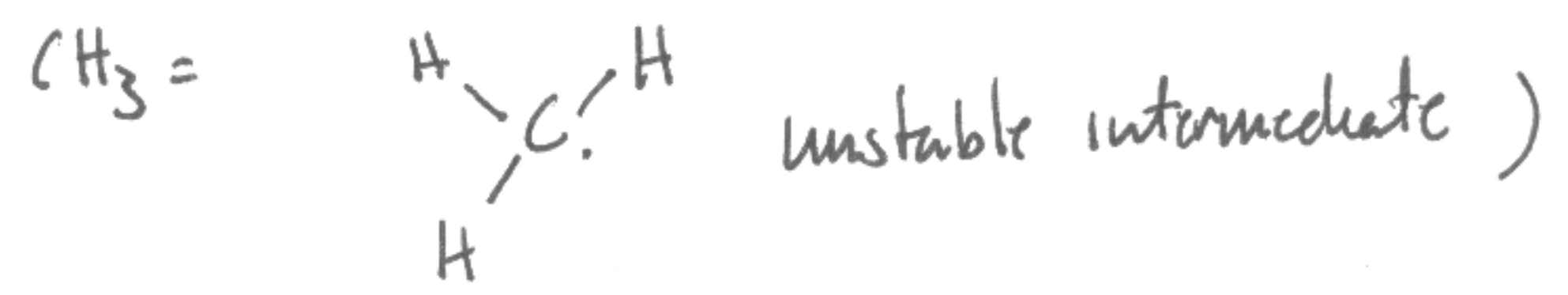
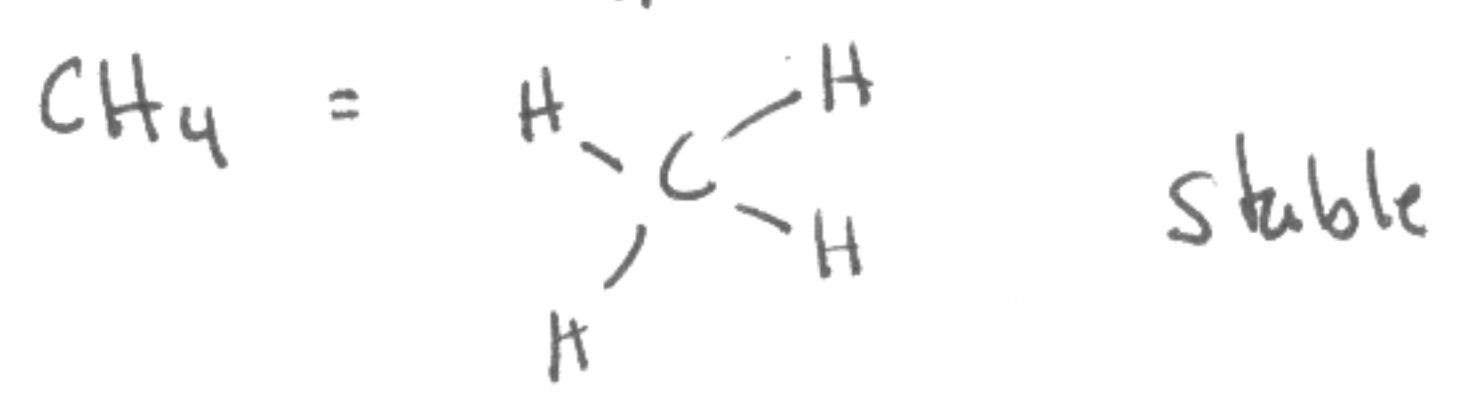
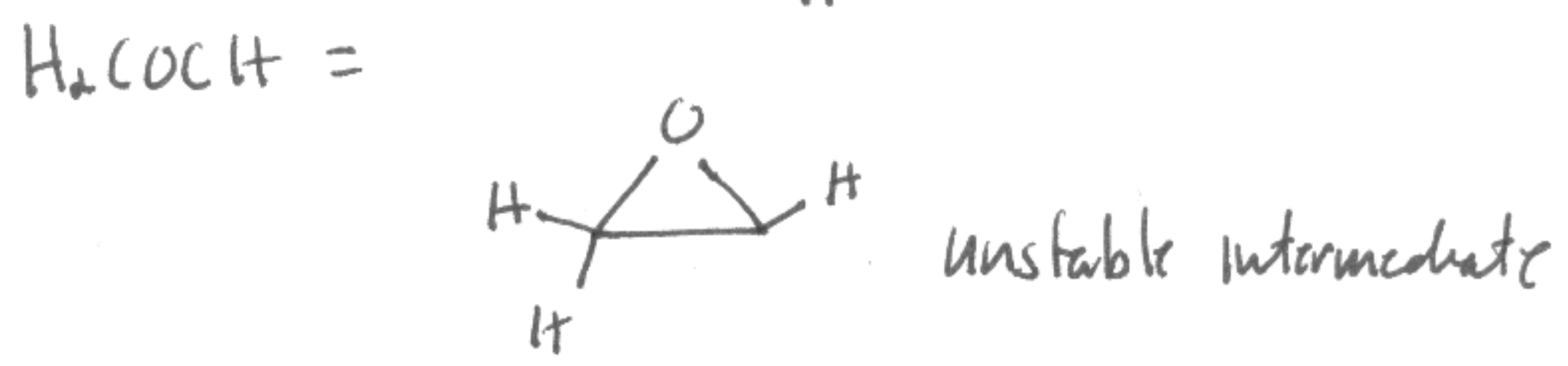
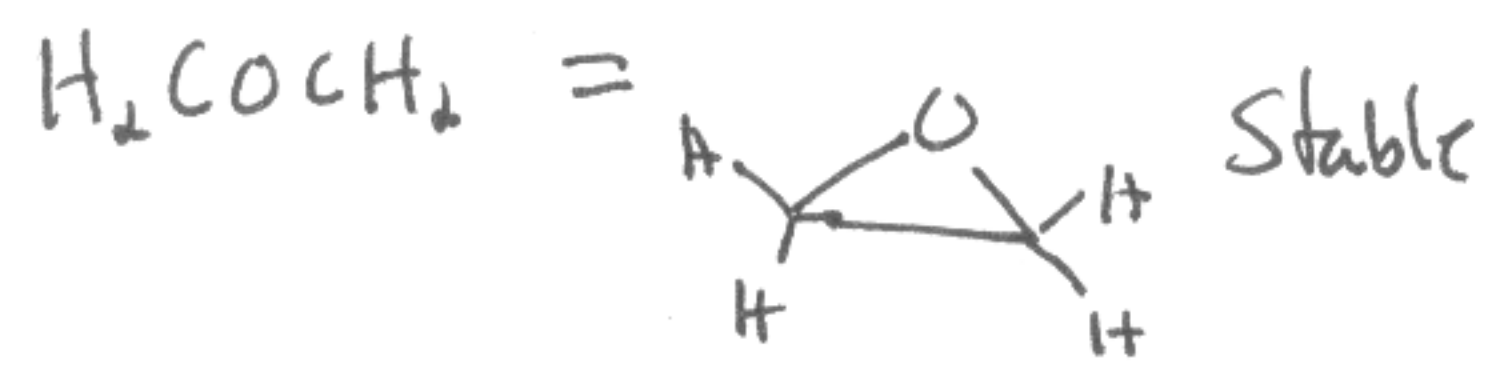
So if we assume SSA and $k_2 \gg k_{-1}$, then this mechanism is correct.

$$\frac{d[\text{N}_2]}{dt} = v(t) = k_1 [\text{H}_2] [\text{NO}]^2 = \text{observed}$$

$$k_{\text{obs}} = k_1$$



(This is one example of how it is important to remember Lewis Structures, even in physical chemistry)



(3)

Write out expression for intermediates:

$$\frac{d[\text{CH}_3]}{dt} = k_2 [\text{H}_2\text{COCH}] - k_3 [\text{CH}_3] [\text{H}_2\text{COCH}_2] - k_4 [\text{CH}_3] [\text{H}_2\text{COH}]$$

$$\frac{d[\text{H}_2\text{COCH}]}{dt} = -k_2 [\text{H}_2\text{COCH}] + k_3 [\text{CH}_3] [\text{H}_2\text{COCH}_2] - k_4 [\text{CH}_3] [\text{H}_2\text{COH}] + k_1 [\text{H}_2\text{COCH}_2]$$

I'm using some judgment here to leave out unphysical rxns. For example although H_2COCH could be created in the back reaction of 2) (i.e. at rate $k_{-2} [\text{CH}_3] [\text{CO}]$), this is much less likely than the forward rxn to form products. So I'm leaving it out. You could leave it in and continue w/ the problem, but sometime you will have to make a simplifying assumption, so might as well do it here.

$$\frac{d[\text{CH}_3]}{dt} = 0 \quad ; \quad \frac{d[\text{H}_2\text{COCH}]}{dt} = 0 \quad ; \quad \frac{d[\text{CH}_3]}{dt} + \frac{d[\text{H}_2\text{COCH}]}{dt} = 0 + 0 = 0$$

by inspection, we see that when we add the two expressions above we get lots of cancellation:

$$\frac{d[\text{CH}_3]}{dt} + \frac{d[\text{H}_2\text{COCH}]}{dt} = 0 = -2k_4 [\text{CH}_3] [\text{H}_2\text{COCH}] + k_1 [\text{H}_2\text{COCH}_2]$$

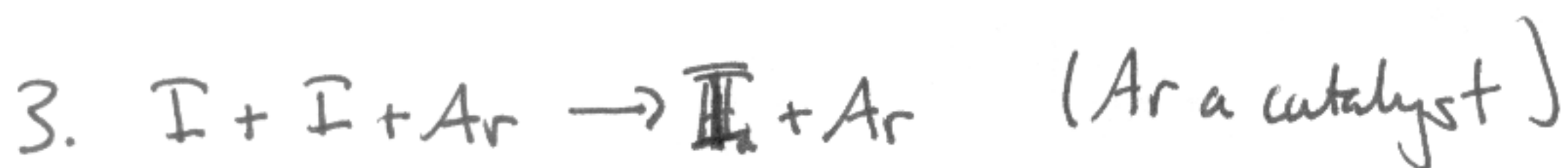
$$\underbrace{[CH_3][H_2COCH]}_{2k_4} = \frac{k_1}{2k_4} [H_2COCH_2]$$

rate of formation of products:

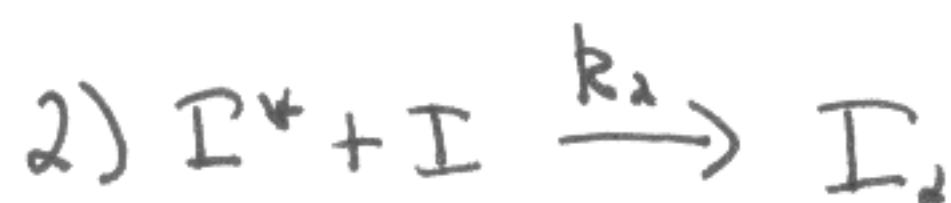
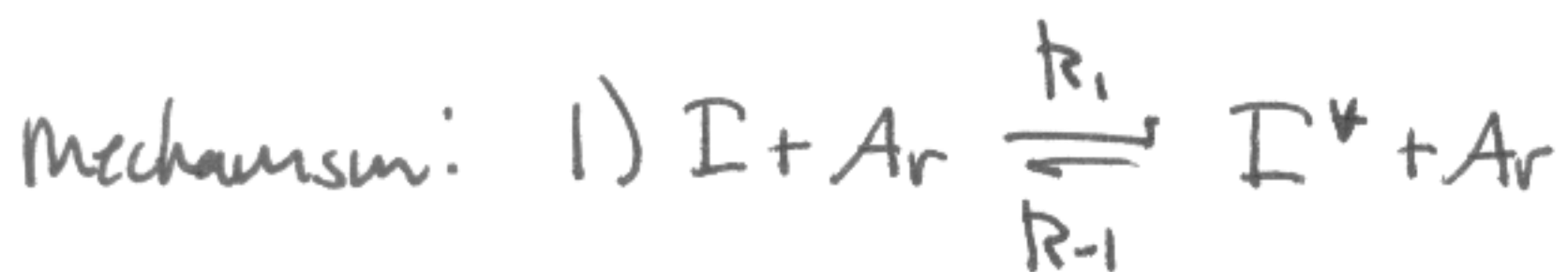
$$\frac{d[product]}{dt} = k_4 [CH_3][H_2COCH]$$

$$\frac{d[product]}{dt} = \cancel{k_4} \left(\frac{k_1}{\cancel{2k_4}} [H_2COCH_2] \right) = \boxed{\frac{k_1}{2} [H_2COCH_2] = v(t)}$$

1st order in H_2COCH_2 , as needed.



$$v(t) = k_{obs} [I][Ar]$$



product: $\frac{d[I_2]}{dt} = k_2 [I^*][I]$

intermediate: $\frac{d[I^*]}{dt} = k_1 [Ar][I] - k_{-1} [I^*][Ar] - k_2 [I^*][I]$

Assume SSA: $\frac{d[I^*]}{dt} = 0$

$$[I^*] = \frac{k_1 [Ar] [I]}{k_{-1} [Ar] + k_2 [I]}$$

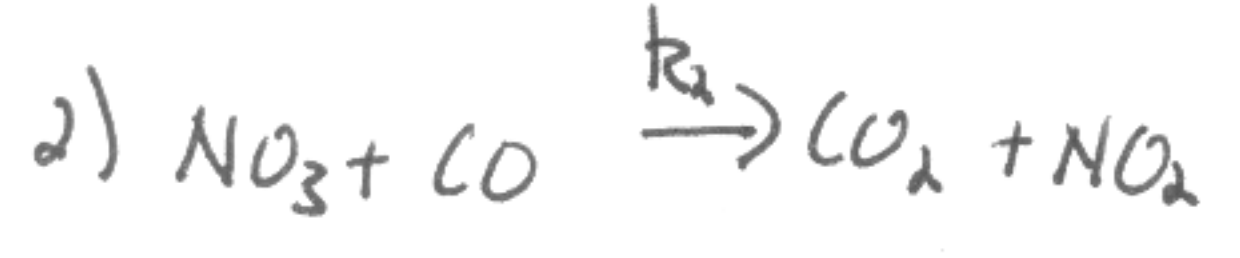
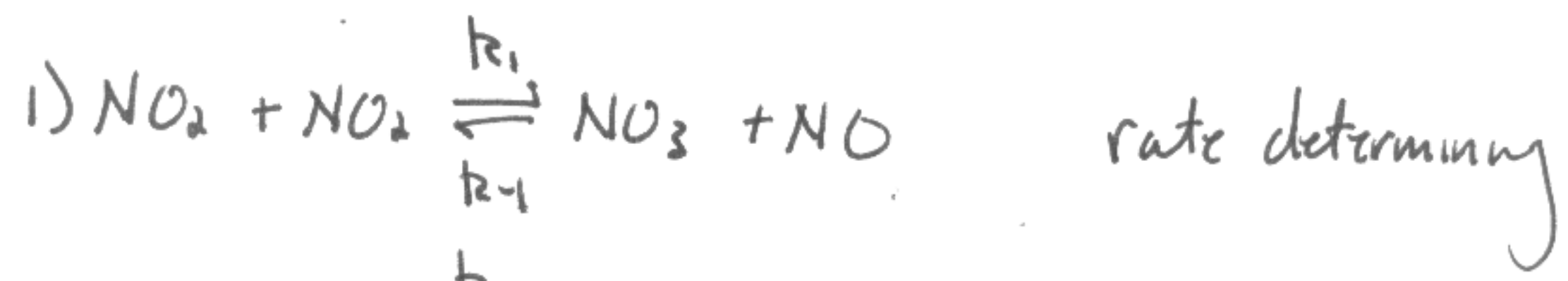
plug into rate: $\frac{d[I_2]}{dt} = k_2 [I] \left(\frac{k_1 [Ar] [I]}{k_{-1} [Ar] + k_2 [I]} \right)$

assume $k_2 \gg k_{-1}$: $\frac{d[I_2]}{dt} = \frac{k_1 k_2 [Ar] [I]^2}{k_2 [I]}$

$v(t) = k_1 [Ar] [I]$ as needed.



$$v(t) = k_{obs} [NO_2]^2$$



$$\frac{d[CO_2]}{dt} = k_2 [NO_3] [CO]$$

$$\frac{d[NO_3]}{dt} = k_1 [NO_2] [NO_2] - k_{-1} [NO_3] [NO] - k_2 [NO_3] [CO]$$

If 1) is rate determining, assume SSA:

$$[NO_3] = \frac{k_1 [NO_2] [NO_2]}{k_{-1} [NO] + k_2 [CO]}$$

By inspection, when we plug this back into $\frac{d[CO_2]}{dt}$, we need

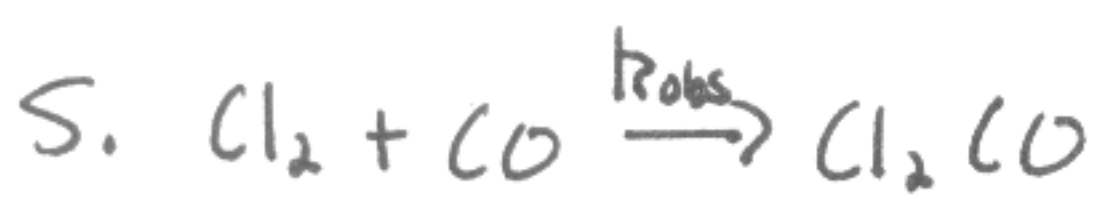
the $[CO]$ to cancel. So we also assume $k_2 \gg k_{-1}$:

$$[NO_3] = \frac{k_1 [NO_2] [NO_2]}{k_2 [CO]}$$

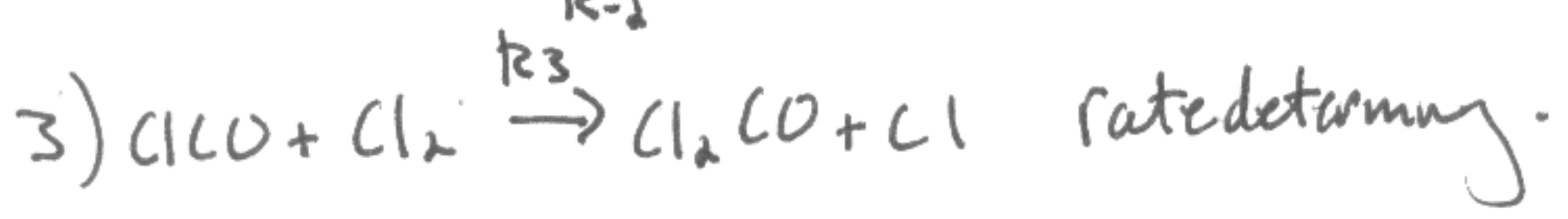
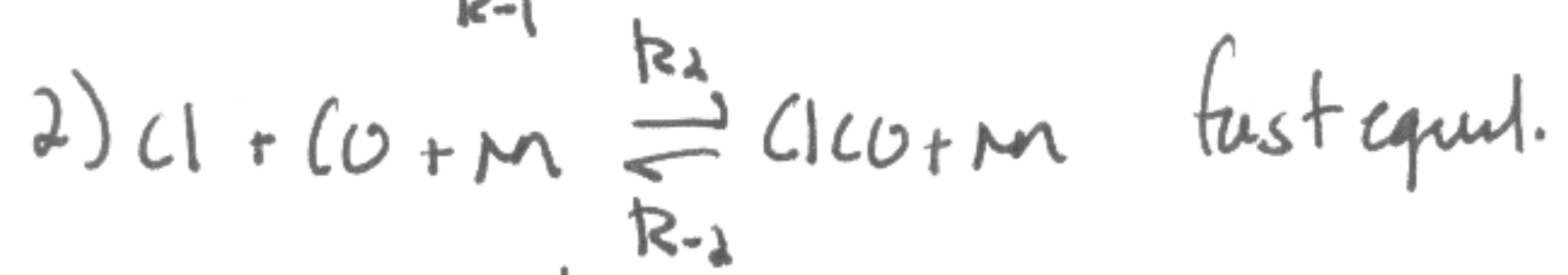
Plug into rate: $\frac{d[CO_2]}{dt} = v(t) = \cancel{k_2 [CO]} \left(\frac{k_1 [NO_2] [NO_2]}{\cancel{k_2 [CO]}} \right)$

$v(t) = k_1 [NO_2]^2$

as needed



$$v(t) = k_{obs} [Cl_2]^{3/2} [CO]$$



(7)

Step ①: $K_{c,1} = \frac{[M][Cl]}{[Cl_2][M]} = \frac{[Cl]^2}{[Cl_2]}$

②: $K_{c,2} = \frac{[ClCO][M]}{[Cl][CO][M]} = \frac{[ClCO]}{[Cl][CO]}$

Solve for intermediates:

$$[Cl] = K_{c,1}^{1/2} [Cl_2]^{1/2}$$

$$[ClCO] = K_{c,2} [Cl][CO]$$

rate: $\frac{d[Cl_2CO]}{dt} = k_3 [ClCO][Cl_2] = v(t)$

plug in $[ClCO]$ and $[Cl]$:

$$v(t) = k_3 K_{c,2} K_{c,1}^{1/2} [Cl_2]^{3/2} [CO]$$

$$R_{obs} = k_3 K_{c,2} K_{c,1}^{1/2} = k_3 \left(\frac{k_2}{k_{-2}} \right) \left(\frac{k_1}{k_{-1}} \right)^{1/2}$$