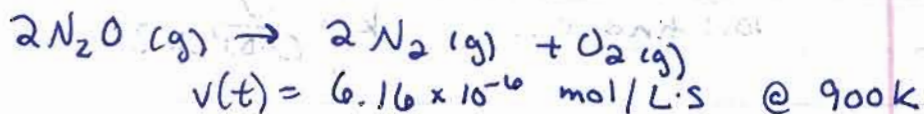


28-2



$$v(t) = -\frac{1}{2} \frac{d[\text{N}_2\text{O}]}{dt} = \frac{1}{2} \frac{d[\text{N}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\frac{d[\text{N}_2\text{O}]}{dt} = -2(6.16 \times 10^{-6}) = -1.23 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$\frac{d[\text{N}_2]}{dt} = 2(6.16 \times 10^{-6}) = 1.23 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

$$\frac{d[\text{O}_2]}{dt} = 6.16 \times 10^{-6} \text{ mol/L}\cdot\text{s}$$

28-8 $\text{NO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{products}$

* use method of initial rates *

$P_0(\text{H}_2)$	$P_0(\text{NO})$	$v_0 \text{ tow/s}$
400	159	34
400	300	125
289	400	160
205	400	110
147	400	79

$$v = k[\text{NO}]^{m_{\text{NO}}}[\text{H}_2]^{m_{\text{H}_2}}$$

$$\frac{125}{34} = \frac{k[300]^{m_{\text{NO}}}[400]^{m_{\text{H}_2}}}{k[159]^{m_{\text{NO}}}[400]^{m_{\text{H}_2}}}$$

$$m_{\text{NO}} = \frac{\ln(34/125)}{\ln(159/300)} \approx 2$$

$$\frac{79}{110} = \frac{k[400]^{m_{\text{NO}}}[289]^{m_{\text{H}_2}}}{k[400]^{m_{\text{NO}}}[205]^{m_{\text{H}_2}}}$$

$$m_{\text{H}_2} = \frac{\ln(110/79)}{\ln(205/289)} \approx 1$$

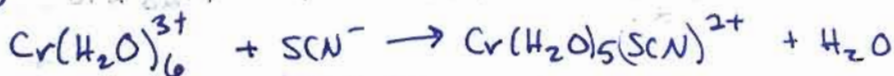
$$V = k[\text{NO}]^2[\text{H}_2]$$

Now find k... $k = \frac{V}{[\text{NO}]^2[\text{H}_2]}$

V_0	34	125	160	110	79
k	3.36×10^{-6}	3.47×10^{-6}	3.46×10^{-6}	3.35×10^{-6}	3.36×10^{-6}

$$k_{\text{ave}} = 3.40 \times 10^{-6} \text{ torr}^{-2} \cdot \text{s}^{-1}$$

28-10



$$V = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}]^{m_{\text{Cr}}}[\text{SCN}^-]^{m_{\text{SCN}}}$$

$$2.11 \times 10^{-11} = k[1.21 \times 10^{-4}]^{m_{\text{Cr}}}[1.05 \times 10^{-5}]^{m_{\text{SCN}}}$$

$$2.82 \times 10^{-11} = k[1.66 \times 10^{-4}]^{m_{\text{Cr}}}[1.02 \times 10^{-5}]^{m_{\text{SCN}}}$$

$$m_{\text{Cr}} = \frac{\ln(2.11 \times 10^{-11} / 2.82 \times 10^{-11})}{\ln(1.21 \times 10^{-4} / 1.66 \times 10^{-4})} \approx 1$$

$$2.11 \times 10^{-11} = k[1.21 \times 10^{-4}]^{m_{\text{Cr}}}[1.05 \times 10^{-5}]^{m_{\text{SCN}}}$$

$$5.53 \times 10^{-11} = k[1.46 \times 10^{-4}]^{m_{\text{Cr}}}[2.28 \times 10^{-5}]^{m_{\text{SCN}}}$$

$$0.382 = 0.8288 (0.4605)^{m_{\text{SCN}}}$$

$$0.461 = (0.461)^{m_{\text{SCN}}}$$

$$m_{\text{SCN}} = 1$$

$$V = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$$

V	2.11×10^{-11}	5.53×10^{-11}	2.82×10^{-11}	9.94×10^{-11}
k	0.0166	0.0166	0.0167	0.0166

$$k_{\text{av}} = 0.0166 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

28-15 1st order rxn $\ln \frac{[A]}{[A]_0} = -k t$

If $[A]_0 = 1$ then $[A] = 0.70$

$\ln(0.70/1) = -k(19.7)$

$k = 1.39 \times 10^{-2} \text{ min}^{-1}$

If $[A]_0 = 1$ then $[A] = 0.145$

$\ln\left(\frac{0.145}{1}\right) = -1.39 \times 10^{-2} t$

$t = 139 \text{ min}$



Plot $\ln [\text{UO}_2(\text{NO}_3)_2]$ vs t ... see attached Excel

ble 1st order

$k = \text{min}^{-1}$



Plot $1/[\text{N}_2\text{O}]$ vs t ... see attached Excel

$k = \text{mol/L}\cdot\text{s}$

28-39 Yes $k = A e^{-E_a/RT}$ so $k + A$ must have same units
 unitless

28-48 $k = A e^{-E_a/RT}$

$\ln k = \ln A - \frac{E_a}{RT}$

$\ln(6.015 \times 10^{-5}) = \ln A - \frac{E_a}{R \cdot 420}$ $\ln(2.971 \times 10^{-3}) = \ln A - \frac{E_a}{R \cdot 470}$

$-9.72 = \ln A - \frac{E_a}{R \cdot 420}$ $-5.87 = \ln A - \frac{E_a}{R \cdot 470}$

$3.8998 = \frac{E_a}{R} \left(\frac{1}{420} - \frac{1}{470} \right)$

$E_a = 95.4 \text{ kJ/mol}$

$A = 4.80 \times 10^{11} \text{ s}^{-1}$

Eqn 28.76...

$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{\Delta H^\ddagger}{RT^2} = \frac{E_a}{RT^2}$

$\Delta H^\ddagger = \Delta U^\ddagger + RT \Delta n^\ddagger$

together... $\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta H^\ddagger}{RT^2}$ or $E_a = RT + \Delta H^\ddagger$

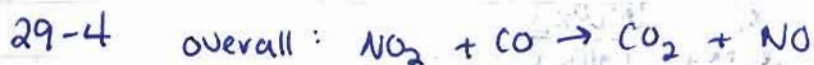
w/ data @ 420K... $\Delta H^\ddagger = 124.4 \text{ kJ/mol}$
 @ 470K... $\Delta H^\ddagger = 124.0 \text{ kJ/mol}$

Use Eq 28.74 to find ΔS^\ddagger ...

$6.015 \times 10^{-5} = \frac{1.38 \times 10^{-23} \cdot 420}{6.626 \times 10^{-34} \cdot 1} e^{-124400/8.314 \cdot 420} e^{\Delta S^\ddagger/R}$

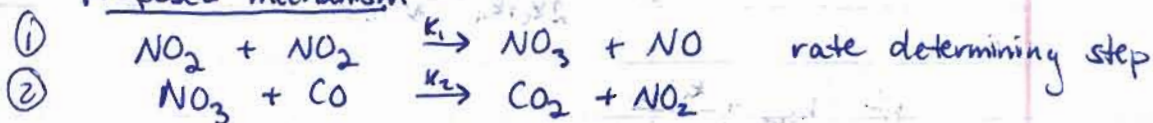
$\ln(0.0203) = \Delta S^\ddagger/R$

$\Delta S^\ddagger = -32.4 \text{ J/mol}\cdot\text{K}$



$$\frac{d[\text{CO}_2]}{dt} = k_{\text{obs}} [\text{NO}_2]^2$$

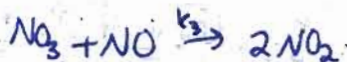
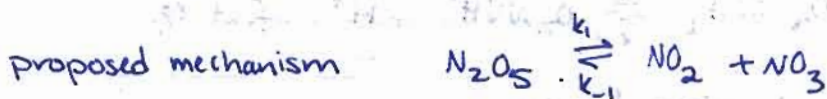
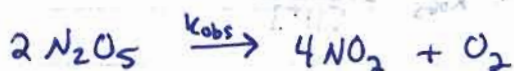
Proposed mechanism



Since ① is rate determining step,

$$\frac{d[\text{CO}_2]}{dt} = k_1 [\text{NO}_2]^2 \quad k_{\text{obs}} = k_1$$

29-11



$$\frac{d[\text{NO}]}{dt} = k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{NO}_3] = 0 \quad \text{S.S.A.}$$

$$k_2 [\text{NO}_2] = k_3 [\text{NO}]$$

$$[\text{NO}] = \frac{k_2 [\text{NO}_2]}{k_3}$$

$$\frac{d[\text{NO}_3]}{dt} = k_1 [\text{N}_2\text{O}_5] - k_2 [\text{NO}_2][\text{NO}_3] - k_{-1} [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}_3][\text{NO}] = 0$$

$$k_1 [\text{N}_2\text{O}_5] = [\text{NO}_3] (k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2] + k_3 [\text{NO}])$$

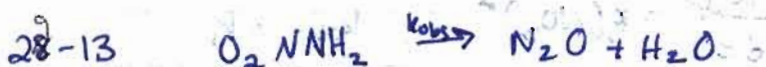
$$[\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2] + k_3 [\text{NO}]} = \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2] + k_2 \frac{k_2 [\text{NO}_2]}{k_3}}$$

$$[NO_3] = \frac{k_1}{2k_2 + k_{-1}} \frac{[N_2O_5]}{[NO_2]}$$

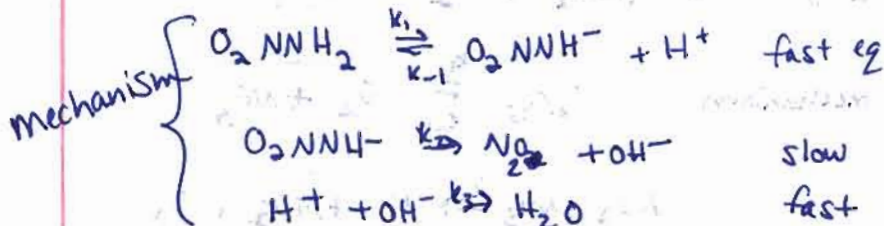
$$\begin{aligned} \frac{d[O_2]}{dt} &= k_2 [NO_2][NO_3] \\ &= k_2 [NO_2] \frac{k_1}{2k_2 + k_{-1}} \frac{[N_2O_5]}{[NO_2]} \end{aligned}$$

$$\text{if } k_{obs} = \frac{k_1 k_2}{2k_2 + k_{-1}}$$

$$\frac{d[O_2]}{dt} = k_{obs} [N_2O_5]$$



$$\frac{d[N_2O]}{dt} = k_{obs} \frac{[O_2NNH_2]}{[H^+]}$$



$$K_c = \frac{k_1}{k_{-1}} = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]} \quad [O_2NNH^-] = \frac{k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

$$\begin{aligned} \frac{d[N_2O]}{dt} &= k_2 [O_2NNH^-] \\ &= \frac{k_2 k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]} \end{aligned}$$

$$\frac{d[N_2O]}{dt} = k_{obs} \frac{[O_2NNH_2]}{[H^+]} \quad k_{obs} = k_2 K_c = \frac{k_2 k_1}{k_{-1}}$$

28-14

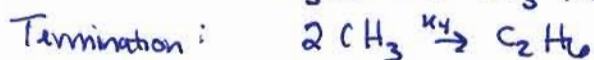
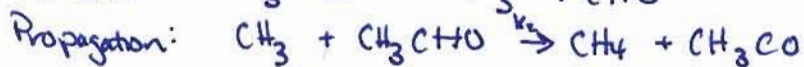
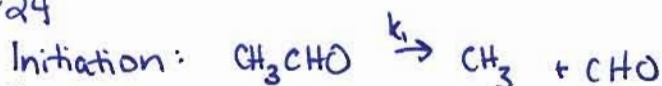
$$\frac{d[\text{O}_2\text{NNH}^-]}{dt} = k_1[\text{O}_2\text{NNH}_2] - k_{-1}[\text{O}_2\text{NNH}^-][\text{H}^+] - k_2[\text{O}_2\text{NNH}^-] = 0$$

$$[\text{O}_2\text{NNH}^-](k_{-1}[\text{H}^+] + k_2) = k_1[\text{O}_2\text{NNH}_2]$$

$$\begin{aligned} \frac{d[\text{N}_2\text{O}]}{dt} &= k_2[\text{O}_2\text{NNH}^-] \\ &= k_2 \frac{k_1[\text{O}_2\text{NNH}_2]}{k_{-1}[\text{H}^+] + k_2} \end{aligned}$$

If $k_2 \ll k_{-1}[\text{H}^+]$, this rate matches that of 28-13.

28-24



$$\frac{d[\text{C}_2\text{H}_6]}{dt} = k_4[\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - k_4[\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}]$$

Steady state for $\text{CH}_3 + \text{CH}_3\text{CO} \dots$

$$\frac{d[\text{CH}_3]}{dt} = 0 = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - k_4[\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = 0 = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}]$$

$$[\text{CH}_3\text{CO}] = \frac{k_2}{k_3}[\text{CH}_3][\text{CH}_3\text{CHO}]$$

$$0 = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] + k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] - k_4 [\text{CH}_3]^2$$

$$[\text{CH}_3] = \left(\frac{k_1}{k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

plug in

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} [\text{CH}_3\text{CHO}]$$

$$= k_2 \left(\frac{k_1}{k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

For presentation (12/12/07)

28-10

29-13

29-14

28-13

[Faint, mostly illegible handwritten notes and equations, possibly representing a reaction mechanism or derivation.]