1 (25 %). Consider the reaction A + 2B → C, with an overall rate law

$$d[C]/dt = k_{obs} [A]^\alpha [B]^\beta$$

(a) The following experimental data are obtained for this reaction:

(i) For $[A]_0 = 1$ M and $[B]_0 = 5.0 \times 10^{-3}$ M,

t(sec)	0	1.0	2.0	3.0	4.0	5.0
[B], (M)	5.0×10^{-3}	4.0×10^{-3}	3.0×10^{-3}	2.0×10^{-3}	1.0×10^{-3}	0

(ii) For $[A]_0 - 1$ M and $[B]_0 - 2$ M, the initial rate $d[C]/dt$ at t $-$ 0 is 0.5×10^{-3} M sec^{-1}

For $[A]_0 = 2$ M and $[B]_0 = 2$ M, the initial rate $d[C]/dt$ at t $= 0$ is 2.0×10^{-3} M sec^{-1}

Question for part (a):

For the rate law above, viz. $d[C]/dt = k_{obs} [A]^\alpha [B]^\beta$, find the orders α and β with respect to reactants A and B respectively, the overall order p, and the effective rate coefficient k_{obs}.

Important note: No detailed fitting or numerical analysis is needed to answer this part! You should be able to obtain the answers by inspection of the data presented above.

From (i) we can gather the following :

$$[A]_0 >> [B]_0 \quad ; \quad -\frac{d[B]}{dt} = 1.0 \times 10^{-3} \, M sec^{-1} \; ; \; \text{independent of } [B]$$
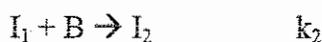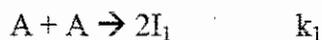
$$\therefore \boxed{\beta = 0}$$

From (ii);

when $[A]_0$ is doubled, $\left(\frac{d[C]}{dt}\right)_{initial} \times \underline{4}$; $\alpha = 2$

$$\boxed{\alpha = 2, \; \beta = 0, \; p = 2}$$

$$\frac{d[C]}{dt} = k_{obs}[A]_0^2 [B]_0^0$$

$$k_{obs} = \frac{d[C]}{dt} \frac{1}{[A]_0^2} = 0.5 \times 10^{-3} M^1 sec^{-1} \left(\frac{1}{(1 M)^2}\right) = \boxed{0.5 \times 10^{-3} M^{-1} sec^{-1}}$$

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(b) The following mechanism

$$A + A \rightarrow 2I_1 \qquad k_1$$

$$I_1 + B \rightarrow I_2 \qquad k_2$$

$$I_2 + B \rightarrow C \qquad k_3$$

has been proposed for this reaction. Answer the following two questions:

(i) Assume that the first step in the mechanism is the rate limiting step, i.e., $k_1 \ll k_2$ and k_3. Write an expression for $d[C]/dt$ in terms of the elementary rate constants k_1, k_2, and k_3 and the concentrations [A] and [B]. You can either give an explicit derivation for your answer or write down the answer and give a clear explanation of why it is correct.

(ii) Given your answer in part (i), is the mechanism consistent with the experimental data in part (a)?

i) explicit derivation:

① $\dfrac{d[C]}{dt} = k_3 [I_2][B]$

use steady-state approximation, because $k_1 \ll k_2, k_3$

$$\frac{d[I_1]}{dt} = k_1 [A]^2 - k_2 [I_1][B] = 0 \quad ; \quad [I_1] = \frac{k_1 [A]^2}{k_2 [B]}$$

$$\frac{d[I_2]}{dt} = k_2 [I_1][B] - k_3 [I_2][B] = 0 \quad ; \quad [I_2] = \frac{k_2 [I_1]}{k_3} = \frac{k_1 k_2 [A]^2}{k_3 k_2 [B]} = \frac{k_1 [A]^2}{k_3 [B]}$$

plug back into ①

① $\dfrac{d[C]}{dt} = k_3 [B]\left(\dfrac{k_1 [A]^2}{k_3 [B]} \right) = k_1 [A]^2$
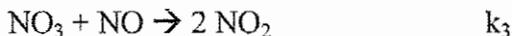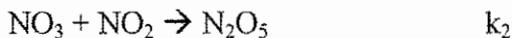
clear explanation; must include rate-limiting step, intermediate species go to 0, $k_2, k_3 \gg k_1$; all I_1 from K_xa l quickly reacts to form $C \rightarrow$ no [B] dependence.

(ii) CONSISTENT W/ EXPERIMENTAL DATA? YES ; $\alpha = 2, \beta = 0$

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2 (25 %). N_2O_5 (g) and NO (g) react to form NO_2 according to the stoichiometric equation

$$N_2O_5 + NO \rightarrow 3\,NO_2 \qquad (g, p = 1\ bar,\ T\ specified)$$

A possible mechanism for this overall reaction is

$$N_2O_5 \rightarrow NO_2 + NO_3 \qquad\qquad k_1$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad\qquad k_2$$

$$NO_3 + NO \rightarrow 2\,NO_2 \qquad\qquad k_3$$

NO_3 is an unstable intermediate.

(a) Obtain expressions for $-d[NO]/dt$ and $-d[N_2O_5]/dt$ in terms of k_1, k_2, k_3, and the concentrations of the stable species N_2O_5, NO, and NO_2.

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_3][NO_2] - \cancel{k_{2}?}$$
$$- k_3[NO][NO_3]$$

$$-\frac{d[NO]}{dt} = k_3[NO_3][NO]$$

$$= \frac{k_1 k_3 [N_2O_5][NO]}{k_2[NO_2] + k_3[NO]} \qquad \text{S.S. appr}$$

$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_2[NO_3][NO_2] \qquad [NO_3] = \frac{k_1[N_2O_5]}{k_2[NO_2] + k_3[NO]}$$

$$= k_1[N_2O_5]\left(1 - \frac{k_2[NO_3][NO_2]}{k_2[NO_2] + k_3[NO]}\right)$$

(b) Simplify the expressions you found in (a) to forms that are valid during the very early stages of the reaction when only a small amount of N_2O_5 and NO have reacted.

Early stages of rxn; $NO_2 \approx 0$ $\qquad [N_2O_5][NO] \gg [NO_2]$

$$-\frac{d[NO]}{dt} = \frac{k_1 k_3 [N_2O_5][NO]}{k_2 \cancel{[NO_2]}^{0} + k_3 [NO]} = k_1[N_2O_5]$$

$$-\frac{d(N_2O_5)}{dt} = k_1[N_2O_5]\left(1 - \frac{k_2[NO_3]\cancel{[NO_2]}^{0}}{k_2\cancel{[NO_2]} + k_3[NO]}\right) = k_1[N_2O_5]$$

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(c) Find the integrated form of the *simplified* rate expression you found in part (b).

$$-\frac{d[NO]}{dt} = -\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$$

FIRST ORDER:
$$\int_{[N_2O_5]_0}^{[N_2O_5]_t} \frac{-d[N_2O_5]}{[N_2O_5]} = \int_{t_0}^{t} k_1 \, t$$

$$\ln[N_2O_5]\Big|_{[N_2O_5]_0}^{[N_2O_5]_t} = -k_1 t$$

$$\boxed{[N_2O_5]_t = [N_2O_5]_0 \, e^{-k_1 t}}$$

(d) Express your result in terms of α, the fraction of N_2O_5 (or of NO) reacted. Assume the initial partial pressures of N_2O_5 and NO are equal, that is, $p_0(N_2O_5) = p_0(NO) = \frac{1}{2} p_0$ (total). Give an expression for α in terms of p(t), the total pressure at time t, and the initial total pressure p_0.

$$\alpha = \frac{P(N_2O_5)_0 - P(N_2O_5)_t}{P(N_2O_5)_0} = 1 - \frac{P(N_2O_5)_t}{P(N_2O_5)_0} = 1 - e^{-k_1 t}$$

$$\boxed{\alpha = 1 - e^{-k_1 t}}$$

$$NO + N_2O_5 \rightarrow 3 NO_2$$

@ t $\quad (1-\alpha \quad 1-\alpha \quad 3\alpha) \, P_0/2$

@ t=0 $\quad (P_0/2 \quad P_0/2 \quad 0)$

$$P_0(N_2O_5) = \frac{P_0}{2}$$
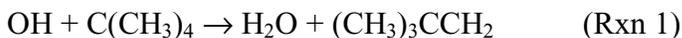
$$P(t) = [2(1-\alpha) + 3\alpha] \frac{P_0}{2}$$

$$P(t) \neq P(N_2O_5)_t$$

$$P(t) = [2+\alpha] \frac{P_0}{2}$$

$$\boxed{2\left(\frac{P(t)}{P_0} - 1\right) = \alpha}$$

5.68J/10.652J Spring 2003 Exam Question 3 with Solution

The literature values for the Arrhenius parameters for

$$OH + C(CH_3)_4 \rightarrow H_2O + (CH_3)_3CCH_2 \qquad \text{(Rxn 1)}$$

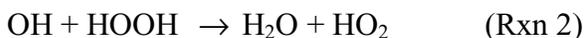$A = 10^9$ liter/mole-second $E_a = 20$ kJ/mole

You are suspicious of these round numbers, and want to check them experimentally. You decide to use HOOH as the precursor to generate the OH radicals by laser flash photolysis. You can get 4 mJ/pulse of 248 nm into the 1 cm^3 reaction volume in your cell, the laser pulse duration is 50 ns, and $\sigma_{248}(HOOH) = 1.6x10^{-20} cm^2$. You will probe the OH by laser induced fluorescence, using optics which collect the light from the $1\, cm^3$ reaction volume in the center of your gas cell.

The apparatus's fluorescence collection/detection efficiency is 1%, so at best the peak

signal will be: $\dfrac{Signal\, Counts}{pulse} = (0.01) * \left(\dfrac{\#\, of\, OH\ formed}{pulse} \right)$

where only the OH formed in the 1 cm^3 volume viewed by the detector contribute to the signal. Note that the percent uncertainty in your determination of the decay time constant τ will be about the same as the percent uncertainty in your signal measured at t = $t_{photolysis} + \tau$.

You are worried that the competing reaction

$$OH + HOOH \rightarrow H_2O + HO_2 \qquad \text{(Rxn 2)}$$

with literature rate parameters

$A = 10^8$ liter/mole-second $E_a = 8$ kJ/mole

may cause difficulties; to minimize them you would like to run under conditions where 90% or more of the OH is consumed by Rxn1 rather than Rxn 2. (You have even less faith in the accuracy of the literature rate parameters for reaction 2 than you do in those for reaction 1, so you do not want your determination of the rate constant for reaction 1 to depend on the exact value of the rate constant for reaction 2.)

For practical reasons you must run your experiment at 1 atm total pressure. You can run at any temperature you want, but because of the instability of HOOH you cannot safely operate at a temperature above 400 K. You can prepare any gas mixtures of HOOH, unreactive He, and C(CH$_3$)$_4$ you desire, with each of the partial pressures accurate to $\pm$ 0.01 atm.

a) What is the algebraic relationship between τ and the rate constants for the reactions?

We expect $[OH]=[OH]_o \exp(-t/\tau)$. After the laser pulse ends, the concentration of OH will satisfy:

$d[OH]/dt = -(k_1[C(CH_3)_4] + k_2[HOOH])[OH]$

plugging in the formula for [OH] in the differential equation, you find

$1/\tau = k_1[C(CH_3)_4] + k_2[HOOH]$

b) If you run at room temperature, how many times larger does the concentration of $C(CH_3)_4$ have to be than the concentration of HOOH to make reaction 1 the dominant loss channel for OH?

Reaction 1 will be dominant if

$k_1(T)[C(CH_3)_4] > k_2(T)[HOOH]$

so we require

$[C(CH_3)_4]/[HOOH] > k_2(T)/k_1(T) = (10^8/10^9) \exp (12 \text{ kJ/mole} / RT)$

at room temperature T = 20 C = 293 K we require

$[C(CH_3)_4]/[HOOH] > 13.8$

c) Give values of T, the partial pressure of HOOH and the partial pressures of $C(CH_3)_4$ that you choose to use to run your experiments to determine the rate constant for Rxn 1, with very brief comments on your choices.

From (b) we know that if we run at room temperature we need
$P(C(CH_3)_4) / P(HOOH) > 13.8$ and we are told that $P_{total} = 1$ atm.
So we know that $13.8*P(HOOH) < P(C(CH_3)_4)$
and $1 \text{ atm} > P(HOOH) + 13.8*P(HOOH)$
i.e. $P(HOOH) < 1 \text{atm} / 14.8 = 0.068$ atm

Now we see a likely problem: our pressure gauge is only good to 0.01 atm, so we will have ~15% uncertainty in P(HOOH) and >1% uncertainty in $P(C(CH_3)_4)$. We can alleviate the problem by running at higher temperature. If we run at the safety limit T=400 K we find $P(C(CH_3)_4) / P(HOOH) > 3.7$ so
$P(HOOH) < 1 \text{ atm} / 4.7 = 0.21$ atm
We don't actually want to run with such a high P(HOOH), since we need room to vary $P(C(CH_3)_4)$. We propose to run at T=400 K with P(HOOH) = 0.08 atm, and $P(C(CH_3)_4)$ from 0.30 up to 0.92 atm. This is enough of a range to see a factor of

two change in τ, and the uncertainty in P(HOOH) will be about 12%, contributing 3-6% to the uncertainty in τ. The uncertainty in P(C(CH₃)₄) will contribute 1-2% to the uncertainty in τ.

    d)   Considering shot noise, compute an upper bound on your signal/noise ratio in a single pulse experiment at one of the conditions you gave in (c).

Signal / Noise from shot noise = (Signal Counts/Pulse)$^{\frac{1}{2}}$

(#OH formed/pulse) < (# 248 nm photons/pulse)(fraction absorbed in 1 cm)
$$< (E_{pulse} / hc/\lambda) [1 - \exp (- \sigma (P(HOOH) N_A/RT) 1 \text{ cm})] = 1.1 \times 10^{14}$$

Signal Counts / Pulse < 0.01 * (# OH formed/ pulse) < 1.1×10^{12}

If you could achieve this peak, you would have phenomenal S/N ~ 10^6.

N.B. In reality, you cannot excite all of the OH's, you are lucky if you excite 0.1% of them. And you want to be able to measure the exponential decays you care about S/N when [OH] has decayed by a factor of 10. So your true S/N is likely more like 10^4. i.e. shot noise contributes an uncertainty of about 0.01% to a measurement of τ.

    e)   If you had an automated data collection instrument that could rapidly average the results from 10,000 experiments, by what factor would your signal/noise ratio improve?

Averaging improves S/N for shot noise (and any other uncorrelated noise sources) by the square root of the number of experiments. So averaging 10,000 experiments improves S/N by a factor of 100.

    f)   In order to determine the rate constant for reaction 1 more accurately, would it be more helpful to buy the automated data collection instrument so you could average 10,000 experiments, or to buy a better gauge for more precisely measuring the partial pressures in the gas mixture?

By part (d) shot noise is not contributing much to our uncertainty, only ~0.01%. But from part (c) the pressure gauge is contributing 2-6%. So it is much more important to buy a new pressure gauge than the averaging electronics.