FCH 511 Homework #05 - Tropospheric Cycling and Ozone Fall 2019

Exercises

A. What is the lifetime of propane in daytime with respect to reaction with OH at 298 K? Assume daytime [OH] = 1.6×10^6 molecule cm^{-3}.

B.1 What are the major sources and sinks of NO_x? (Chapter 2)

B.2 What is the fate of $CH_3OO\bullet$ in the absence of NO_x?

C. Using the spreadsheet on the course website for computing termolecular rate constants, compute the effective 2nd order rate constant for $OH + NO_2 \rightarrow HONO_2$ at:

a. 1 atm, 298 K **b.** 1 atm, 250 K **c.** 50 km

D. What is the steady-state concentration of each organic radical in the mechanism below? [ethane]= 2 ppbv, [OH]= 1×10^6 molecules cm^{-3}, [NO]= 0.1 ppbv, P_{total} = 1 atm , and T=298 K.

1) $C_2H_6 + OH \rightarrow \bullet C_2H_5 + HOH$	k_1 (in *Burkholder*)
2) $\bullet C_2H_5 + O_2 \rightarrow C_2H_5OO\bullet$	k_2 (Table 2 of *Burkholder*)
3) $C_2H_5OO\bullet + NO \rightarrow C_2H_5O\bullet + NO_2$	k_3 (in *Burkholder*)
4) $C_2H_5O\bullet + O_2 \rightarrow CH_3CH{=}O + HOO\bullet$	k_4 (in *Burkholder*)

E. The Figure on the page 2 is from a paper by J. A. Thornton, et al., in the *Journal of Geophysical Research D*, 2002 (DOI:10.1029/2001JD000932). The x-axis is time in fraction of a day, so a difference of 0.2 corresponds to 0.2 days (4 hours and 48 minutes). The results come from a measuring station at ground level outside of Nashville, Tennessee.

What is the rate of production of O_3 from NO_2 photolysis at t= 190.6?

What is the ratio of $J(NO_2)$ to $J(O_3)$ towards the middle of the day?

H. What are the likely reactions of the following alkoxy radicals in 1 atm of air at 298 K under rural conditions in the daytime?

$CH_3(CH_2)_5CH_2O\bullet$ $CH_3CH_2CH_2O\bullet$ $CH_3(CH_2)_5C(CH_3)_2O\bullet$

I. At what altitude (to the nearest 5-10 km) is the reaction ClO + ClO closest to the low-pressure limit?

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Problems

1.A. Calculate the rate at which O_3 is produced from ethane oxidation to $CH_3CH=O$.
Assume the OH + ethane reaction is the rate limiting step in ozone production from ethane.
[OH] = global daytime average, ground level, 298 K, and [ethane] = 1.8 ppbv.

1.B. What does Exercise B.2 say about whether the assumption, above, is valid?

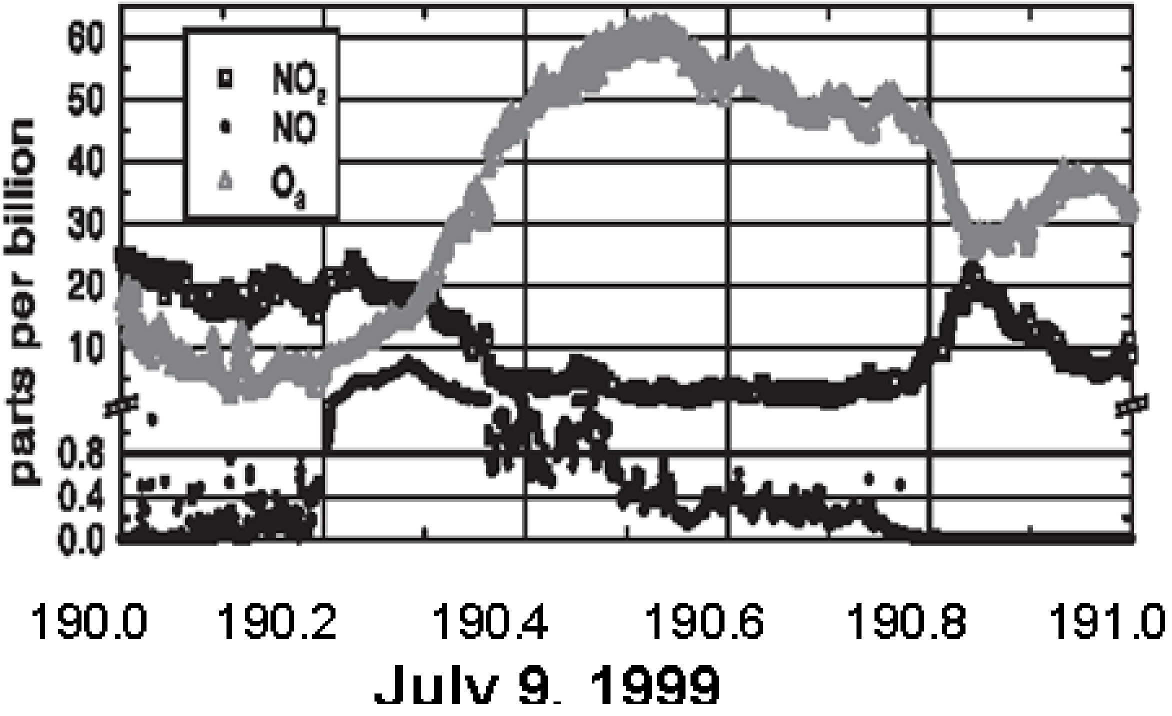
1.C. What other termination reaction can cause the assumption to be invalid?

2. Sketch out the fates of the organic species formed in the degradation of $C(CH_3)_4$ in polluted air during the day (initiated by OH) with rural NO_x concentrations.
Follow all *significant* branches until all *organic* species are converted to non-radicals.
Include $ROO\bullet + NO \rightarrow RONO_2$

3. Use the Figure below …

3.1. together with a ruler and calculator to determine $d[NO_2]/dt$ (the **net** rate of production of NO_2) at t= 190.**9**. Do not use rate constants. Turn in the Figure with lines drawn.

3.2. together with the results of Exercise C to calculate the total production (molecule cm^{-3} = rate × time) of $HONO_2$ over the course of the daytime. Assume [OH] averages 0.3 pp**t**v and $[NO_2]$ averages 6 pp**b**v during the daytime.



Part of my goal of this Homework was for you to learning the mechanism of degradation of organic compounds and applying your kinetics skills to those mechanisms. Another part was to:

- remind you of some basic calculus
- remind you how to do a trend analysis without a computer