**1.84/12.807 Problem Set 1**

## 1) Thermal dissociation of PAN

Peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$) is an important temporary reservoir for nitrogen oxides ($NO_x$), and as such allows for the transport of $NO_x$ far from its original source. It is formed by the termolecular reaction of peroxyacetyl radical ($CH_3C(O)OO$) with $NO_2$ (rxn 1a); one of its main loss processes is unimolecular dissociation back to reactants (rxn 1b):

$$CH_3C(O)OO + NO_2 + M \rightarrow CH_3C(O)OONO_2 + M \qquad (1a)$$

$$CH_3C(O)OONO_2 + M \rightarrow CH_3C(O)OO + NO_2 + M \qquad (1b)$$

a) Using the JPL recommendation, plot the rate constant for PAN thermal dissociation (reaction 1b) as a function of temperature (180-300K) at 760 Torr. Plot k in log space.

b) Again, using the JPL recommendations, plot the rate constant for PAN thermal dissociation (reaction 1b) as a function of pressure at 298 K. Pressure should be plotted in Torr, spanning a large enough pressure range to show the transition from the low- to the high-pressure limit. Plot both P and k in log space.

## 2) Photolysis of PAN

PAN can photolyze via two major channels:

$$CH_3C(O)OONO_2 + h\nu \rightarrow CH_3C(O)OO + NO_2 \qquad (2a)$$

$$\rightarrow CH_3C(O)O + NO_3 \qquad (2b)$$

a) Calculate $J_{PAN}$ for typical ground-level, summertime conditions (1 atm, 298K). Use actinic fluxes from S&P (Table 4.3), and the IUPAC recommendations for photochemical parameters.

b) Plot $\sigma(\lambda)$, $I(\lambda)$, and $J(\lambda)$ vs $\lambda$, illustrating the wavelength range over which PAN absorbs.

## 3) Lifetime of PAN vs. altitude

a) Plot the lifetimes of PAN with respect to thermal decomposition (reaction 1b), photolysis (reaction 2), and reaction with OH (reaction 3), as well as the overall PAN lifetime, as a function of altitude, between ground level and 10 km.

$$CH_3C(O)OONO_2 + OH \rightarrow \text{products} \qquad (3)$$

At all altitudes, assume $[OH] = 2\times10^6$ molec/cm$^3$. You will need values of pressure and temperature as a function of altitude, which you can get from a "Standard Atmosphere" table (S&P Table A.8); in lecture 6 we'll discuss how to roughly calculate these. For simplicity you may assume that $\sigma(\lambda)$ and $I(\lambda)$ are temperature- and altitude-independent.

b) What does this plot tell you about the processes controlling PAN in the troposphere?

c) Qualitatively (no calculations!), in what ways did assuming that $\sigma_{PAN}$ and $I(\lambda)$ are independent of temperature and altitude introduce errors in your calculation of photolytic lifetimes?