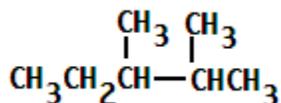


CHM 5423 – Atmospheric Chemistry

Exam 2 - Due date: Thursday, April 8th (by 11:59pm). Please turn in your exam by sending it to me at my FIU email address joensj@fiu.edu. Indicate in your email that you are sending me your Exam 2 solutions.

There are six problems on this exam. Do all of the problems. Show your work.

1) Consider the alkane $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$, shown below



a) Based on the method discussed in class (and used in problem 4 of problem set 3), find the bimolecular rate constant for the reaction of the above molecule with OH radical at $T = 298 \text{ K}$. Also find the percentage of each initial alkyl radical formed in the reaction.

b) Assuming an average concentration of OH radical $[\text{OH}] = 1.0 \times 10^6 \text{ molecule/cm}^3$, estimate the half-life for the above molecule in the troposphere. Assume $T = 298 \text{ K}$ and use your value for k found in part a in finding the value for $t_{1/2}$.

c) Bimolecular rate constants for the alkane + OH reaction are usually obtained from experiment. However, it is common to use the above method to find the percentage of each alkyl radical formed by reaction. Explain this observation.

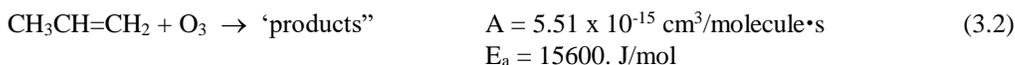
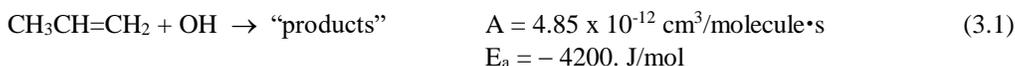
2) For each of the following reactions give the most likely initial products of the reaction. Assume $p = 1.00 \text{ atm}$ and $T = 298 \text{ K}$.



c) $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{O}_3 \rightarrow$ (give the initial ozonide that forms and the most likely products formed when the ozonide decomposes).



3) In the daytime propene ($\text{CH}_3\text{CH}=\text{CH}_2$) reacts with hydroxyl radical (OH) and ozone (O_3). The two reactions that take place are:



The rate constant for the above reactions obeys the Arrhenius equation for the range of temperatures found in the troposphere. Values for A and E_a for each reaction have therefore been given above.

a) The activation energy for reaction 3.1 is negative. What, if anything, does this tell you about the mechanism for the reaction?

b) Find the half-life of propene in the troposphere, and the fraction of propene molecules that react with hydroxyl radical and with ozone. Assume $p = 1.00 \text{ atm}$, $[\text{OH}] = 1.0 \times 10^6 \text{ molecule/cm}^3$, and $[\text{O}_3] = 1.0 \times 10^{12} \text{ molecule/cm}^3$. Do your calculation for $T = 288 \text{ K}$ and $T = 240 \text{ K}$.

c) Why might the above results be misleading in regards to the fate of propene emitted at night?

4) The rate constant for the gas phase reaction of nitrogen dioxide with ozone



is $k = A \exp(-E_a/RT)$, where $A = 1.2 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}$ and $E_a = 20400. \text{ J/mol}$.

- The daytime concentration of NO_3 in the troposphere is approximately zero. Explain this observation.
- As discussed in class, at night NO_3 concentrations slowly increase over time due to reaction 4.1. Find the concentration of NO_3 in the troposphere (in ppb) at $t = 3, 6, 9,$ and 12 hours after sunset for the following set of initial conditions: $p_{\text{total}} = 1.00 \text{ atm}$, $[\text{O}_3] = 40. \text{ ppb}$, $[\text{NO}_2] = 0.40 \text{ ppb}$, $T = 280. \text{ K}$. Assume $[\text{NO}_3] = 0.00 \text{ ppb}$ at $t = 0$ hours. Give your NO_3 concentrations in units of ppb. State any assumptions made in your calculation.
- The actual night time concentrations of NO_3 are likely lower than that predicted above. Why would you expect that to be the case?

5) The following questions have to do with the paper by Kumar et al. (2021). "Experimental and computational investigations of the tropospheric photooxidation reactions of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol initiated by OH radicals and Cl atoms" *J. Phys. Chem. A* **125**, 523-535. One of the reactions studied was



- Why is this an interesting reaction for atmospheric chemists to study?
- Based on our discussion of tropospheric reactions, there are two radicals likely to form from reaction 5.1. What are they? Which do you think is more likely to form? Why?
- In the experiments by Kumar and coworkers OH radicals were generated by the process



Light from a 248 nm laser was used to carry out the photodissociation process in reaction 5.2. Assuming all of the excess energy from the reaction appears as translational energy of the OH radicals, and that the energy is equally divided between the two radicals, what is the average kinetic energy of the radicals that are produced? What temperature does this correspond to?

- Kumar and coworkers assume in their experiments that the temperature at which reaction 5.1 takes place is the temperature of the bath gas in the Pyrex reaction chamber, even though the OH radicals produced by reaction 5.2 have a different effective temperature than that of the bath gas. Why is this a reasonable assumption?
- Figure 1 of the paper gives the results obtained by the relative rate method for reaction 5.1 at $T = 298. \text{ K}$. Explain how the rate constant for reaction 5.1 was obtained from the information in the figure.

6) The Leighton mechanism is the following set of reactions



a) Assuming the Leighton mechanism is correct, find $[\text{NO}]$ and $[\text{NO}_2]$ for the following set of conditions.

$$\begin{array}{ll} [\text{NO}_x] = 10.0 \text{ ppb} & k_1 = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecule}\cdot\text{s} \\ [\text{O}_3] = 60.0 \text{ ppb} & J_2 = 1.3 \times 10^{-3} \text{ s}^{-1} \\ [\text{air}] = 2.0 \times 10^{19} \text{ molecule/cm}^3 & k_3 = 6.0 \times 10^{-34} \text{ cm}^6/\text{molecule}^2\cdot\text{s} \end{array}$$

b) Assuming no other reactions involving NO, NO₂, and O₃ are significant, what is the value for the half life for NO and NO₂ for the above set of conditions?

c) Why are the above half life value for NO and NO₂ misleading?

d) Assuming that reactions 6.2 and 6.3 are the only significant reactions forming and removing oxygen atoms from the troposphere, find the steady-state concentration of oxygen atoms in the troposphere. Give your final answer in units of atoms/cm³.

Solutions.

1) a) The overall rate constant can be found as follows.

Primary hydrogens = 12

Secondary hydrogens = 2

Tertiary hydrogens = 2

$$\begin{aligned} \text{So } k &= 12 (0.45 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) + 2 (4.7 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) + 2 (19.5 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) \\ &= 53.8 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s} \end{aligned}$$

There are six possible initial products of the reaction

	Percentage
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2\text{CH}_2\text{CH}-\text{CHCH}_3 \end{array}$	$3 (0.45)/53.8 \times 100\% = 2.5 \%$
$\begin{array}{c} \text{CH}_2 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCH}_3 \end{array}$	$3 (0.45)/53.8 \times 100\% = 2.5 \%$
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_2 \\ \quad \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCH}_3 \end{array}$	$6 (0.45)/53.8 \times 100\% = 5.0 \%$
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}-\text{CH}-\text{CHCH}_3 \end{array}$	$2 (4.7)/53.8 \times 100\% = 17.5 \%$
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2\text{C}-\text{CHCH}_3 \end{array}$	$1 (19.5)/53.8 \times 100\% = 36.2 \%$
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2\text{CH}-\text{C}-\text{CH}_3 \end{array}$	$1 (19.5)/53.8 \times 100\% = 36.2 \%$

b) The pseudo-first order rate constant is $k' = (53.8 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) (1.0 \times 10^6 \text{ molecule}/\text{cm}^3)$

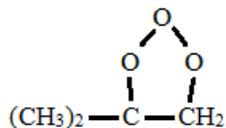
$$= 5.38 \times 10^{-6} \text{ s}^{-1}$$

And so $t_{1/2} = \frac{\ln(2)}{5.38 \times 10^{-6} \text{ s}^{-1}} = 1.29 \times 10^5 \text{ s} = 35.8 \text{ hours}$

c) It is relatively easy to experimentally measure the rate constant for the alkane + OH reaction by a variety of methods, such as the relative rate method, and so the overall rate constant can be found. Finding the branching ratios for each possible product for the reaction is more difficult, as the products are highly reactive. If each possible initial product has its own unique final stable product this can sometimes be done, but it is not easy (or even likely).

2) Note there are several possible initial products. I am only asking for the one most likely to form.

- a) $(\text{CH}_3)_2\text{CCH}_3 + \text{H}_2\text{O}$ loss of tertiary hydrogen
- b) $(\text{CH}_3)_2\text{CCH}_2\text{OH}$ addition to form the more stable radical
- c) initial ozonide



- $(\text{CH}_3)_2\text{COO} + \text{H}_2\text{CO}$ more stable Criegee biradical
- d) $\text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$ only abstraction product
- e) $\text{CH}_3\text{C}=\text{O} + \text{HNO}_3$ aldehydic proton is easier to remove

3) a) The collision theory model for reactions suggests activation energies must be positive (or zero) for a direct reaction. A negative activation energy indicates the reaction likely takes place in several steps, which can lead to negative activation energies for the overall rate constant even when those for the individual steps in the mechanism are all positive.

b) We need the individual rate constants at each temperature. We also need to find the pseudo-first order rate constants, which are the values for the bimolecular rate constant multiplied by either $[\text{OH}]$ or $[\text{O}_3]$. The overall rate constant for removal is the sum of the individual pseudo-first order rate constants. The fraction of the reaction proceeding by each pathway is k'/k'_{total} , and the half-life is $t_{1/2} = \ln(2)/k'_{\text{total}}$.

T = 288 K

OH reaction	$k_{\text{OH}} = 2.80 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$	$k'_{\text{OH}} = 2.80 \times 10^{-5} \text{ s}^{-1}$	$f = 0.77$
O_3 reaction	$k_{\text{O}_3} = 8.16 \times 10^{-18} \text{ cm}^3/\text{molecule}\cdot\text{s}$	$k'_{\text{O}_3} = 8.16 \times 10^{-6} \text{ s}^{-1}$	$f = 0.23$
		$k'_{\text{total}} = 3.62 \times 10^{-5} \text{ s}^{-1}$	$t_{1/2} = 5.32 \text{ hour}$

T = 240 K

OH reaction	$k_{\text{OH}} = 3.98 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$	$k'_{\text{OH}} = 3.98 \times 10^{-5} \text{ s}^{-1}$	$f = 0.95$
O_3 reaction	$k_{\text{O}_3} = 2.22 \times 10^{-18} \text{ cm}^3/\text{molecule}\cdot\text{s}$	$k'_{\text{O}_3} = 2.22 \times 10^{-6} \text{ s}^{-1}$	$f = 0.05$
		$k'_{\text{total}} = 4.20 \times 10^{-5} \text{ s}^{-1}$	$t_{1/2} = 4.58 \text{ hour}$

Unlike most reactions, the half-life is shorter at the lower temperature due to the dominance of the addition reaction in the removal of propene from the troposphere.

c) At night, the OH addition reaction will not occur, and so all of the reaction will proceed by addition of O_3 . The fraction of reaction taking place by the O_3 addition reaction will therefore be larger. However, the O_3 addition reaction is sufficiently slow that not all the propene will react away at night ($t_{1/2,\text{O}_3} = 23.6$ hours at T = 288 K) so both reactions will end up being important in the removal of propene from the troposphere.

4) a) NO_3 can photodissociate by the absorption of visible photons, and it has a strong absorption spectrum in the visible region. The quantum yield for photodissociation is ~ 1 for $\lambda < 600$ nm, and is significant at longer wavelengths. Therefore, any NO_3 formed quickly photodissociates to regenerate the reactants, preventing any buildup of NO_3 in the daytime.

b) At $p = 1.00$ atm, $T = 280$. K, $[\text{air}] = 2.62 \times 10^{19}$ molecule/ cm^3 .

So initially we have

$$[\text{O}_3] = 40. \text{ ppb} = 1.05 \times 10^{12} \text{ molecule}/\text{cm}^3$$

$$[\text{NO}_2] = 0.40 \text{ ppb} = 1.05 \times 10^{10} \text{ molecule}/\text{cm}^3$$

The rate constant for reaction 4.1 is $k_{4.1} = 1.88 \times 10^{-17} \text{ cm}^3/\text{molecule}\cdot\text{s}$.

Since $[\text{O}_3] \gg [\text{NO}_2]$, we can assume pseudo-first order conditions, and so

$$k'_{4.1} = k_{4.1} [\text{O}_3] = (1.88 \times 10^{-17} \text{ cm}^3/\text{molecule}\cdot\text{s}) (1.05 \times 10^{12} \text{ molecule}/\text{cm}^3) = 1.97 \times 10^{-5} \text{ s}^{-1} = 0.0711 \text{ hr}^{-1}.$$

If we assume the only process forming NO_3 is reaction 4.1, and no additional introduction of NO_2 into the troposphere, then

$$[\text{NO}_3]_t = [\text{NO}_2]_0 \{ 1 - e^{-k't} \} \quad [\text{NO}_2]_0 = 0.40 \text{ ppb} \quad k' = 0.0711 \text{ hr}^{-1}$$

t (hr)	$[\text{NO}_3]_t$ (ppb)
3	0.077
6	0.139
9	0.189
12	0.229

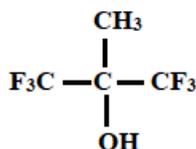
c) It is difficult to assess the assumption of no additional NO_2 into the troposphere at night, but since transportation (cars, trucks) are the major source of NO_x in urban atmospheres, and there are far fewer cars and trucks in operation at night, this would be a reasonably good assumption for an urban area.

However, we have ignored the effect of the reaction

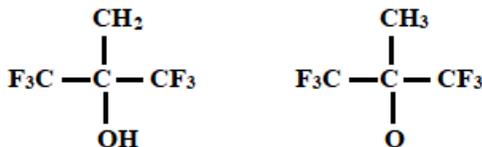


That would act to reduce both $[\text{NO}_2]$ and $[\text{NO}_3]$, particularly as NO_3 built up at night, and so lead to lower than expected NO_3 concentrations.

5) a) The molecule 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HF2M2P, shown below) is a possible replacement for CFCs in air conditioners, refrigerators, and other such applications. HF2M2P is more reactive in the troposphere than CFCs (due to the presence of abstractable H atoms) and so will have a shorter half-life, reducing its effect as a greenhouse gas. Since it contains no Cl atoms, it should not destroy ozone in the stratosphere even if a small amount of the compound migrates there. Measurement of the rate constant for the HF2M2P + OH reaction will make it possible to find the half-life for the molecule in the troposphere.



b) There are two types of abstractable hydrogens and so two possible initial products from the reaction with OH, as shown below



Based on comparison with other alcohol molecules I would expect the product at left to be more likely to form. For what its worth, the Kumar paper comes to the same conclusion based on high level calculations.

c) For the process

$$\begin{aligned}
 \text{H}_2\text{O}_2 \rightarrow 2 \text{OH} \quad \Delta H^\circ_{\text{rxn}} &= 2 \Delta H^\circ_f(\text{OH}) - \Delta H^\circ_f(\text{H}_2\text{O}_2) \\
 &= 2(37.49) - (-135.51) = 210.5 \text{ kJ/mol}
 \end{aligned}$$

where we have use the thermochemical data from JPL-19. On a per molecule basis this is 3.50×10^{-19} J/molecule.

$$\text{For a 248 nm photon, } E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{(248. \times 10^{-9} \text{ m})} = 8.01 \times 10^{-19} \text{ J}$$

For one mole of photons, this is $N_A (hc/\lambda) = (6.022 \times 10^{23} \text{ mol}^{-1})(8.01 \times 10^{-19} \text{ J}) = 482.4 \text{ kJ/mol}$

So the excess energy above what is needed to break the O-O bond is $E = E_{\text{photon}} - E_{\text{bond}}$

$$= (482.4 - 210.5) = 272.0 \text{ kJ/mol}$$

If we assume all of that energy ends up as kinetic energy in the OH radicals produced, and that it is equally distributed between each radical, then $E_K(\text{OH}) = (272.0 \text{ kJ/mol})/2 = 136.0 \text{ kJ/mol}$

But the average translational kinetic energy of a gas molecule is $E_K = 3RT/2$.

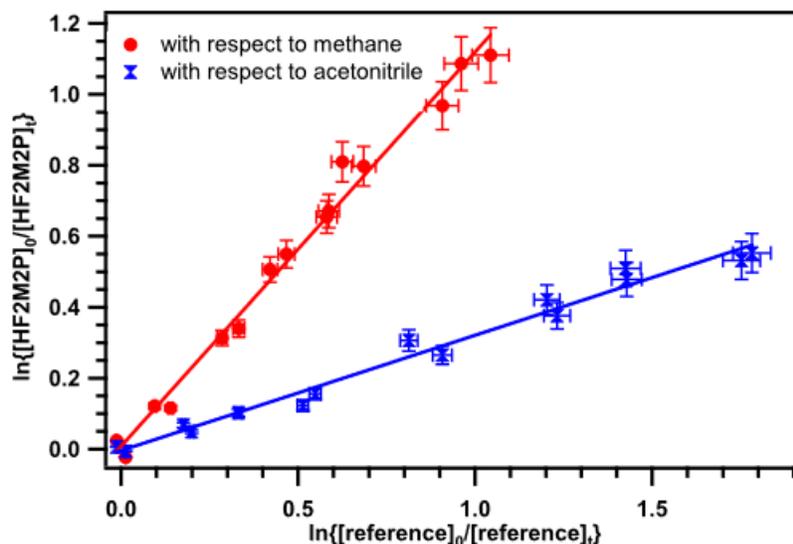
$$\text{So } T = 2E_K/3R = (2 \cdot 272000. \text{ J/mol}) / (3 \cdot 8.3145 \text{ J/mol}\cdot\text{K}) = 21800. \text{ K}$$

So the “effective temperature” of the OH radicals produced from photodissociation by the laser is 21800 K.

d) The experiments were carried out at 760 torr, with the concentration of HF2M2P and reference compound at $\sim 4 \times 10^{16}$ molecule/cm³. At T = 300 K, 760 torr of bath gas (N₂) is $[\text{N}_2] = 2.5 \times 10^{19}$ molecule/cm³.

Since $[\text{N}_2]/[\text{HF2M2P}] = (2.5 \times 10^{19}) / (4 \times 10^{16}) \cong 600$, the OH radicals produced by photodissociation will on average collide with several hundred bath molecules before encountering a HF2M2P or reference molecule. This should give the OH radicals a chance to thermalize to the temperature of the bath gas.

e) Figure 1 from the paper is given below.



Based on the relative rate method, $k_{5.1} = k_{\text{ref}} (\text{slope,ref})$, where k_{ref} is the rate constant for the reaction of the reference compound with OH, and (slope,ref) is the slope found from the above plot.

6) a) We expect a steady state concentration for NO_2 , and so .

$$\frac{d[\text{NO}_2]}{dt} = 0 = k_1 [\text{NO}] [\text{O}_3] - J_2 [\text{NO}_2]$$

So $\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{J_2}{k_1 [\text{O}_3]}$ $[\text{O}_3] = (60.0 \times 10^{-9}) (2.0 \times 10^{19} \text{ molecule/cm}^3) = 1.2 \times 10^{12} \text{ molecule/cm}^3$
 $[\text{NO}_x] = (10.0 \times 10^{-9}) (2.0 \times 10^{19} \text{ molecule/cm}^3) = 2.0 \times 10^{11} \text{ molecule/cm}^3$

$$\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{1.3 \times 10^{-3} \text{ s}^{-1}}{(1.8 \times 10^{-14} \text{ cm}^3/\text{molecule}\cdot\text{s}) (1.2 \times 10^{12} \text{ molecule/cm}^3)} = 0.0602$$

So $[\text{NO}] = 0.0602 [\text{NO}_2]$

$$[\text{NO}_x] = [\text{NO}] + [\text{NO}_2] = 0.0602 [\text{NO}_2] + [\text{NO}_2] = 1.0602 [\text{NO}_2]$$

$$[\text{NO}_2] = \frac{[\text{NO}_x]}{1.0602} = \frac{10.0 \text{ ppb}}{1.0602} = 9.43 \text{ ppb} = 1.89 \times 10^{11} \text{ molecule/cm}^3$$

$$[\text{NO}] = 0.0602 [\text{NO}_2] = (0.0602) (9.43 \text{ ppb}) = 0.57 \text{ ppb} = 1.1 \times 10^{10} \text{ molecule/cm}^3$$

b) For NO, the pseudo-first order rate constant is $k'_1 = k_1 [\text{O}_3]$

$$= (1.8 \times 10^{-14} \text{ cm}^3/\text{molecule}\cdot\text{s}) (1.2 \times 10^{12} \text{ molecule/cm}^3)$$

$$= 0.0216 \text{ s}^{-1} \quad t_{1/2} = 32. \text{ s}$$

$$\text{For } \text{NO}_2, t_{1/2} = \ln(2)/J_2 = \ln(2)/(1.3 \times 10^{-3} \text{ s}^{-1}) = 533. \text{ s} (= 8.9 \text{ min})$$

c) These half-life values are misleading since all that happens in the Leighton mechanism is transformation of NO_x into NO or NO_2 . Whatever NO or NO_2 is lost by one step in the mechanism is regenerated by another step in the mechanism, and so total NO and NO_2 concentrations are unchanged.

d) If the only source of O atoms in the troposphere is from the Leighton mechanism, then we can assume a steady state concentration of O atoms, given by

$$\frac{d[\text{O}]}{dt} = 0 = J_2 [\text{NO}_2] - k_3 [\text{O}] [\text{O}_2] [\text{M}]$$

$$[\text{O}] = \frac{J_2 [\text{NO}_2]}{k_3 [\text{O}_2] [\text{M}]} \quad \text{Since the fraction of air that is } \text{O}_2 \text{ is } 0.209, \text{ then } [\text{O}_2] = 0.209 [\text{M}]$$

$$\begin{aligned} \text{So } [\text{O}] &= \frac{(1.3 \times 10^{-3} \text{ s}^{-1})(1.89 \times 10^{11} \text{ molecule/cm}^3)}{(6.0 \times 10^{-34} \text{ cm}^6/\text{molecule}^2 \cdot \text{s})(0.209)(2.0 \times 10^{19} \text{ molecule/cm}^3)^2} \\ &\cong 5000 \text{ atoms/cm}^3 \end{aligned}$$

This is small (~ 200 times smaller than the typical OH concentration in the troposphere), and so would be difficult to measure directly. In addition, the transitions $^3\text{P} \rightarrow ^1\text{D}$ and $^3\text{P} \rightarrow ^1\text{S}$ are dipole forbidden and so weak, making detection by absorption or fluorescence even more of a challenge.

However, $\text{O}(^3\text{P})$ has recently been detected in the mesosphere/thermosphere of the Earth (Richter, H., et al., (2021) Direct measurements of atomic oxygen in the mesosphere and lower thermosphere using terahertz heterodyne spectroscopy. Comm. Earth Environ. 2, 1-9). <https://www.nature.com/articles/s43247-020-00084-5>

Of course, atomic oxygen concentrations in this region of the atmosphere is much higher than in the troposphere.