November CUME

Department of Chemistry
University of Missouri—Columbia
Friday, November 22, 1996
@ one O'Clock
Chemistry Reading Room

Dr. Rainer Glaser

Announced Reading

"My Life with O_3, NO_x, and Other YZO_x Compounds (1995 Nobel Lecture)"
Paul J. Crutzen *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1758-1777.

"Polar Ozone Depletion (1995 Nobel Lecture)"
Mario J. Molina *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1779-1785.

"Stratospheric Ozone Depletion by Chlorofluorocarbons (1995 Nobel Lecture)"
F. Sherwood Rowland *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1787-1798.

Question 1. Ozone - Structure, Electronic Structure and Measurement. (30 points)

(a) Draw the Lewis structures of **dioxygen** (the "normal" oxygen molecule) and of **ozone**. If resonance plays a role, then provide all of the important resonance structures. Indicate whether ozone is linear or nonlinear. For each molecule state its preferred **spin multiplicity**. For dioxygen, state whether the Lewis structure does or does not correctly reflect that dioxygen is paramagnetic. (8 p.)

(b) How is ozone generated in the stratosphere? Give a **reasonable estimate** of the wavelength of the light needed in the photolytic process. Hint: State what type of excitation occurs and then use your general knowledge of UV/Vis spectroscopy to come up with a good guess. (4 p.)

(c) What property makes stratospheric ozone so immensely valuable to us humans? In your answer explain the term "ozone cutoff" and provide a reasonable estimate for its value. (6 p.)

(d) Provide an explanation for your answers to parts **(b)** and **(c)** using simple MO theory. In other words, explain with MO theory why the _____ (red, blue) shift occurs in the **absorption** in going from O_2 to O_3. Use orbital energy diagrams in your explanation. (2 p. for red/blue, 10 for theory)

Question 2. Ozone Destruction Routes. (20 points)

Berkeley's Harold Johnston wrote in a Science article in 1971 that "... oxides of nitrogen from SST [supersonic stratospheric transport vehicles] exhaust pose a much greater threat to the ozone layer than does the increase in water. ...".

The chain reaction by which **nitrogen monoxide catalyzed** destruction of ozone.

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

overall: $O_3 + O \rightarrow 2\ O_2$

The chain reaction by which **water catalyzed** destruction of ozone.

$HO + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O_3 \rightarrow HO + 2\ O_2$

overall: $2\ O_3 \rightarrow 3\ O_2$

The chain reaction by which **chlorine atom catalyzed** destruction of ozone.

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

overall: $O_3 + O \rightarrow 2\ O_2$

(a) The oxygen species that drives the chain reaction by which **water** catalyzes the destruction of ozone is NOT water itself but the hydroxyl radical. How is this **actual catalyst** produced from water? Be precise about the multiplicity of the excited states involved in these reactions. (4 p.)

(b) One of the catalyzed processes is quite different from the purely photochemical destruction of ozone while the other two catalyzed processes and the purely photochemical ozone destruction are quite similar! State which one of the catalyzed ozone destruction chains may occur in the dark and which one can only occur with light. (2 p.)

(c) We discussed the chain reactions by which chlorine and hydroxyl radicals can destroy ozone. In addition to these molecules' individual efforts at destroying ozone, their chemistry is linked via the formation of HOCl. Provide reactions that show both the formation and the decomposition of HOCl. Also provide the overall reaction. (4 p.)

(d) Given the **homolytic bond dissociation energies** of Cl_2 (58 kcal/mol) and of H_2O_2 (51 kcal/mol), can you make any statement about the respective homolytic bond dissociation energy of HOCl? Guide: **Pauling's definition of electronegativity** should somehow show up in your answer! (10 points)

Question 3. NO Removal. (20 points)

(a) The actual rate of ozone depletion caused by chlorine atom and nitrogen monoxide is significantly less than the combined effects of their individual ozone destruction abilities. Hence, Cl and NO somehow must interact with each other with the result of annihilation of their ozone destruction capabilities. What reactions between Cl and NO are thought to be responsible for the reduction in ozone destruction ability? (5 points)

(b) Write Lewis structures for the nitrogen oxides NO, NO_2, NO_3 and N_2O_5. For each of these molecules, specify what symmetry point group would be most likely (a good description of geometry without the correct point group symbol would be fine). (10 points)

(c) Describe how HNO_3 is formed from NO and O_3. (5 points)

Question 4. Chlorofluorocarbons and the Man-Made Ozone-Destroying Chain. (15 points)

(a) Explain why CCl_3F undergoes photolytic decomposition in the higher atmosphere but not in the lower atmosphere. Show the decomposition reaction. Give a reasonable estimate as to where (at what height) the decomposition becomes significant. (5 points)

(b) Draw a **perspective** structure of the molecule Cl_2O_2. (5 p.)

(c) Describe the chain of events that causes chlorine atoms to initiate fast ozone depletion under cold, sunlit stratospheric conditions. Be specific as to which reaction in the sequence is the photoreaction. (5)

Question 5. Ozonolysis in the Laboratory. (15 points)

Consider the conversion of 6-methyl-1-heptene into 5-methylhexanal via ozonolysis. Draw the structures of the starting material, of the molozonide initially formed, of the ozonide subsequently formed, and of the product. Specify reagents and conditions (T, solvent).