The cume announcement placed the "Focus of National Chemistry Week, October 19 - 25, 2003, on the topic "Earth's Atmosphere" which was exposed at http://www.chemistry.org and the following two reviews were recommended reading.

Abundant Oxygenates in the Atmosphere: A Biochemical Perspective Fall, R. *Chemical Reviews* **2003,** (Review) ASAP Article. DOI: 10.1021/cr0206521

Laboratory Perspectives on the Chemical Transformations of Organic Matter in Atmospheric Particles Rudich, Y. *Chemical Reviews* **2003**, ASAP Article. DOI: 10.1021/cr020508f

(1) Biogenic emissions are measured in the unit **Tg of C yr^{-1}**. State what each of the abbreviations in the unit means. (5 points)

(2) The **biogenic emission of methanol** is estimated to be about 100 Tg of C yr^{-1}. Explain what this number means; e.g. relate the amount to something we might be able to imagine. Basically, I am asking you to demonstrate some sort of evidence of your understanding of the magnitude of the emission. (10 points)

(3) According to the review by Fall, **pectin biosynthesis** constitutes the main source of biogenic **methanol**. In general terms, explain how that works in principle. What type of compound is pectin? Where does it occur in nature? How does pectin lead to the production of methanol? (10 points)

(4) According to the review by Fall, the anoxic **fermentative metabolism** of flood-tolerant plants constitutes the main source of biogenic **acetaldehyde**. In general terms, explain how that works in principle. What is pyruvic acid? From what plant materials is the pyruvic acid made? How does pyruvic acid lead to the production of acetaldehyde? (10 points)

(5) According to the review by Fall, **cyanogenic plants** are the main source of biogenic **acetone**. HCN is the plants' chemical weapon. Explain as best as you can, how plants "store" the HCN bullets, how plants "activate" their HCN weapon, and how the activation of the weapon is "triggered." Conceptual insights will received credit; structural details (e.g. key features of linmarin) are desirable. (15 points)

(6) According to the review by Rudich, ozone is taken up by organic areosols via a "reactive uptake" and this simply means that the ozone reacts with the organics in the aerosol. In the review, the reaction of ozone with terminal alkenes is discussed in some detail (Figure 10). First, write down the standard Criegee mechanism for ozonolysis. In aerosols, the main difference is that the primary ozonide falls apart and that no recombination occurs! Explain how the **diradical R-CH_2-CH-O-O** can decay to form an aldehyde, an acid, or an alkane. (25 points)

Criegee mechanism for reaction of ozone with propene:
Diradical R-CH_2-CH-O-O to aldehyde:
Diradical R-CH_2-CH-O-O to acid:
Diradical R-CH_2-CH-O-O to alkane:

(7) We usually think of NO and of NO_2 as the oxides of nitrogen. Yet, there also is NO_3 in the atmosphere. Draw a Lewis structure of NO_3. Suggest what NO_3 might do if it encountered an alkane, e.g. decane. (10 points)

(8) In section 3.5.9. on "Uptake of Cl and Br by Organic Surfaces", it is written: "High concentrations of Cl and Br, ~105 and ~106 atoms cm^3, respectively, are estimated for marine environments where high organic aerosol concentrations are also expected. The reactive uptake of Cl and Br atoms by closely packed organic thin films was studied in a low-pressure flow reactor by Moise and Rudich.

The uptake coefficients due to reactive uptake by SAM of alkene were measured at room temperature and in the presence of oxygen and are shown in Table 3. For Br, = (3 ± 1) Å~ 10-2 for an alkane surface and = (5 ± 2) Å~ 10-2 for alkene surfaces. Cl was more reactive with 0.1. The processing of the surface was monitored using FTIR, XPS, and contact angle measurements. Surface-bound products were determined, and changes in the surface hydrophobicity were measured. The contact angles of water decreased by more than 50 following the reaction, indicating a substantial change in surface order, morphology and hydrophobicity. The IR vibrational lines of C=C, CH_3, and CH_2 which were observed clearly by direct IR absorption prior to exposure nearly completely disappeared."

Given this information, suggest a reasonable reaction mechanism for the reaction of chlorine atom with 1-octene. (15 points)