

which the ozone production is  $\text{NO}_x$ -limited. For example, reducing the concentration of VOCs from 1.2 ppm to 0.8 ppm has virtually no effect on the ozone concentration, which remains at 160 ppb since the curve in this region is almost linear and runs parallel to the horizontal axis. However, a reduction of the  $\text{NO}_x$  level, from about 0.03 ppm at point A to a little less than half this amount by dropping down to the curve directly below it, cuts the predicted ozone level in half, from 160 ppb to 80 ppb.

**PROBLEM 3-6**

Using Figure 3-2, and assuming a  $\text{NO}_x$  concentration of 0.20 ppm, estimate the effect on ozone levels of reducing the VOC concentration from 0.5 to 0.4 ppm. Do your results support the characterization of that zone of the graph as “VOC-limited”?

Some urban areas such as Atlanta, Georgia, and others located in the southern United States incorporate or border upon heavily wooded areas whose trees emit enough reactive hydrocarbons to sustain smog and ozone production even when the concentration of **anthropogenic** hydrocarbons, that is those which result from human activities, is low. Deciduous trees and shrubs emit mainly the gas isoprene, whereas conifers emit pinene and limonene; all three hydrocarbons contain  $\text{C}=\text{C}$  bonds. In urban atmospheres, the concentration of these compounds normally is much less than that of the anthropogenic hydrocarbons and it is not until the latter are reduced substantially that the influence of these natural substances becomes noticeable. In areas affected by the presence of vegetation, then, only the reduction of emissions of nitrogen oxides will reduce photochemical smog production substantially.

Recent research has shown that some of the smog in Mexico City originates from butenes that are a minor component of the liquefied gas that is purchased by many residents and used for cooking and heating in their homes, and some of which apparently leaks into the air.

Although hydrocarbons with  $\text{C}=\text{C}$  bonds are the most reactive type in photochemical smog processes, others play a significant role after the first few hours of a smog episode have passed and the concentration of free radicals has risen. For this reason, control of emissions of *all* VOCs is required in areas with serious photochemical smog problems. Gasolines, which are a complex mixture of hydrocarbons, are now formulated in order to reduce their evaporation, since gasoline vapor has been found to contribute significantly to atmospheric concentrations of hydrocarbons. The control of VOCs in air is discussed in more detail in Chapter 5. New regulations in California (with Los Angeles especially in mind) limit the use of hydrocarbon-containing products such as barbeque starter fluid, household aerosol