TROPOSPHERIC CHEMISTRY OF NATURAL HYDROCARBONS, ALDEHYDES, AND PEROXY RADICALS: THEIR CONNECTIONS TO SULFURIC ACID PRODUCTION AND CLIMATE EFFECTS.

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Natural hydrocarbons are oxidized in the atmosphere to form a variety of oxygenated organic species, including aldehydes and peroxy radicals (Finlayson-Pitts and Pitts, 1986; Gaffney et al., 1987; Gaffney and Marley, 1992). Isoprene (a C-5 hydrocarbon) and the monoterpene hydrocarbons (C-10 species) are the major organic compounds emitted from deciduous and coniferous forests, respectively. Isoprene emissions are known to be dependent on solar radiation and temperature, consistent with stomatal resistance and daytime photosynthetic production. Thus, isoprene emissions are diurnal, with negligible nighttime emissions, and are typically larger than emissions of the monoterpenes, in accord with their vapor pressures. In contrast, the monoterpenes are emitted throughout the day and night, with monoterpene concentrations typically reaching maximum values at night (Yokouchi and Ambe, 1988).

Recent work has shown that natural hydrocarbon emissions can significantly affect the levels of urban and regional tropospheric ozone (Chameides et al., 1990). Here we review the reactivities of these biogenic trace gases, particularly isoprene, focusing on their importance in the production of aldehydes and peroxy radicals, leading to increased levels of hydrogen peroxide over regional forests. Hydrogen peroxide can lead to the wet oxidation of sulfur dioxide to acidic sulfate in aerosols, fogs, and clouds. In turn, acidic sulfate can act to as a light scattering aerosol and a source of cloud condensation nuclei (CCN), potentially leading to global cooling (Charlson et al., 1992). Aerosol sulfate and other dissolved organic and inorganic compounds can also play important roles as a greenhouse species in the lower troposphere (Marley et al. 1993).

Isoprene Chemistry

Isoprene is a naturally occurring C-5 diene. As a hemiterpene, it is also a biochemical building block for the monoterpenes and higher terpenoid compounds found in plants. The principal emitters of isoprene are deciduous hardwood forests (oaks, maples, etc.). Because of its greater volatility, as compared to the C-10 monoterpenes, isoprene emissions correlate quite strongly with the photosynthetic activity of plants. Thus, emissions of isoprene follow a diurnal pattern of high release during the daylight hours and little or no release during the night. Emissions of isoprene also correlate with temperature and relative humidity. Since the major source of isoprene emissions is deciduous trees, isoprene emissions into the troposphere are seasonal, with high levels emitted during the spring and summer and negligible emission during the winter, when trees are dormant.

Hydroxyl and Peroxy Radicals from Isoprene Oxidation

Hydroxyl radical is formed by the reaction of $O(^1D)$ atoms with water in the troposphere. The electronically excited oxygen atoms are produced during ozone photolysis by ultraviolet-B (uv-B) radiation. Isoprene reacts quite rapidly with OH radical during the daytime hours via addition reactions to form methyl vinyl ketone and methacrolein. These compounds in turn are oxidized by OH in the atmosphere to form a variety of

compounds. A major portion of the isoprene carbon reacts to form formaldehyde, a key species in the atmosphere and a source of hydroperoxyl radicals (HO_2). As outlined previously (Gaffney et al. 1987; Chameides et al., 1990), isoprene oxidation reactions can increase levels of regional and urban ozone, because of the formation of HO_2, RO_2, and RCO_3 radicals during isoprene photooxidation in the presence of nitrogen oxides. Here R designates a number of generic organic functional groups produced during isoprene photooxidation, the simplest being methyl (CH_3). In the case of isoprene, many of the initial peroxy radicals are produced from the addition of OH followed by reaction with molecular oxygen (Finlayson-Pitts and Pitts, 1986).

The initial source of OH is photochemical reactions (e.g. ozone photolysis) that are driven by uv-B radiation. If uv-B radiation is increased because of depletion of stratospheric ozone, then the oxidation reactions of isoprene and other natural hydrocarbons are likely to increase in the presence of energy-related pollutants (i.e. NO_x). These oxidation reaction pathways are highly dependent on the levels of NO_x.

The Importance of NO Levels - O_3 versus H_2O_2

Under conditions of high NO, peroxyl radicals formed by the oxidation of isoprene react with NO to form nitrogen dioxide, which in turn photolyses to form ozone and reactive OH and RO radicals. These reactive radicals serve to catalytically cycle NO to NO_2 without destroying ozone and thus lead to elevated ozone production.
Under conditions of low NO, the HO_2 radical can react with itself to form hydrogen peroxide or with RO_2 or RCO_3 radicals to form organic hydroperoxides and peracids, respectively.

Tradeoffs - Ozone or Sulfate

Depending upon the levels of NO present in the region, isoprene oxidation reactions will lead to increased ozone and hydrogen peroxide levels (Gaffney et al., 1987). Hydrogen peroxide can react in the aqueous phase with SO_2 to form sulfuric acid, leading to increased levels of aerosol sulfate. The aqueous phase oxidation of sulfur dioxide is much more rapid than gas-phase oxidation by OH radical. The lifetime of SO_2 with respect to OH reaction is approximately 13 days (Finlayson-Pitts and Pitts, 1986), whereas the aqueous-phase reaction with hydrogen peroxide can lead to a high percent of conversion to sulfate per hour.

Both ozone and sulfate are key environmental pollutants involved in acid precipitation, plant damage and stress, and global climate forcing. Ozone is a greenhouse gas in the troposphere, while aerosol sulfate has been proposed to be radiatively important as a light scatterer, as a key source of CCN, and as a long-wave absorber of radiation (Charlson et al., 1992; Kiehl and Briegleb, 1993; Marley et al. 1993). Thus, the chemical interactions of isoprene with energy-related pollutants such as NO_x and SO_2 can lead to increased levels of oxidants and acidic aerosols and can act affect local cloud chemistries and physics (Gaffney and Marley, 1992).

Tropospheric Pollution - Biosphere Feedbacks

The emissions of reactive hydrocarbons from the biosphere are not constant. Indeed, the emission rates and composition depend on a number of variables including the health of the plant, light intensities, temperature, and nutrient availability (Gaffney and Marley, 1991). Thus, chemical modeling that attempts to address the interactions of biogenic gases with energy-related pollutants will need to evaluate feedbacks between tropospheric pollution and the biosphere. A diagram of some of these feedbacks is given in Figure 1.

For example, increases in greenhouse gases like ozone over deciduous forests due to isoprene-NO_x
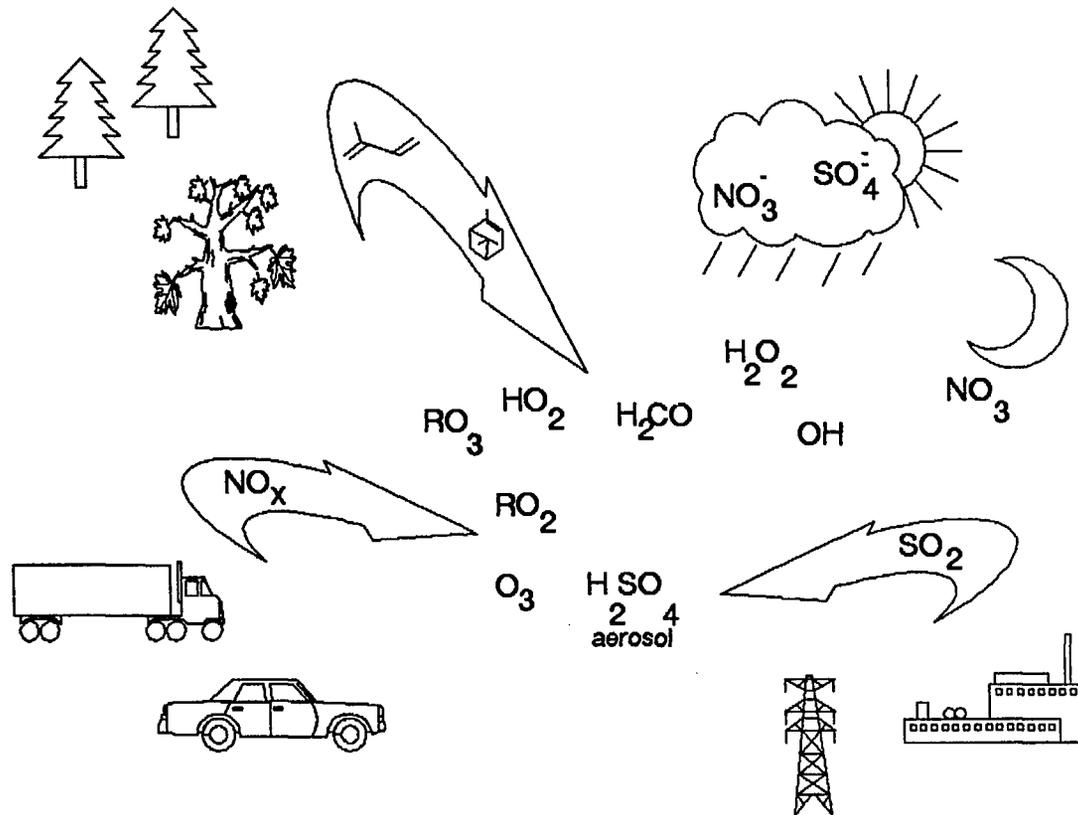
Figure 1. Schematic representation of some of the key chemical interactions of energy-related pollutants with natural reactive hydrocarbons, leading to the production of aldehydes, peroxy radicals, peroxides, ozone, and sulfuric acid aerosols.

photochemical interactions could lead to increased temperatures and increased emissions of isoprene. Ozone in turn can act as a phytotoxin, reducing the ability of trees to produce isoprene as the plant is stressed by the oxidant. Increased levels of sulfate might change the types and persistence of clouds over the ecosystem, affecting precipitation, light intensity, and temperature and again changing the emission rates of isoprene and other biogenic trace gas species. Wet deposition of acidic nitrate and sulfate can supply nutrients to many forested areas that are nutrient limited, again affecting the production of biogenic trace gases. Future modeling studies are needed to examine these feedbacks, if we are to adequately assess regional ozone control and acid rain control strategies as they relate to each other and to climate effects (Gaffney and Marley, 1991; Gaffney and Marley, 1992).

Seasonal effects can also be important. Sulfate and formaldehyde levels over the Blue Ridge Mountains are much higher during the summer than during the winter (Gaffney et al., 1987). This observation is consistent with the fact that >70% of the forests in this region are deciduous. Thus, isoprene emissions are essentially shut off during the winter when deciduous trees are dormant, reducing the formation of formaldehyde, hydrogen peroxide, and the rate of sulfate oxidation.

Monoterpenes

Monoterpenes are highly reactive with ozone, OH, and nitrate radical. Table 1 summarizes half-lives calculated for reactions of propylene, isoprene, and selected monoterpenes with OH, O_3, and NO_3 radical. Lifetimes were calculated by assuming a concentration for OH of 1 x 10^6 molecules cm^{-3}, for ozone, 60 ppbV, and for nitrate radical, 20 parts per trillion (Finlayson-Pitts and Pitts, 1986). As indicated before, production of OH is photochemical and is therefore a daytime loss mechanism.
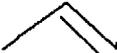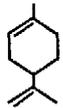
Ozone reactions occur during the day and night. Nitrate radical (NO_3) is formed from the reaction of ozone and nitrogen dioxide. Because it is rapidly photolyzed, NO_3 is effective in the oxidation of organics only during the nighttime. Nitrate radical addition reactions can lead to the formation of organic nitrates, while abstraction reactions lead to the formation of nitric acid and peroxy radicals (Finlayson-Pitts and Pitts, 1986).

In contrast to isoprene, monoterpenes are known to be emitted continuously, with their highest concentrations in forested canopies observed during the night (Yokouchi and Ambe, 1988). Because they are larger organic molecules, many monoterpenes form large oxygenated acids, peracids, keto-acids, ozonides, and other heavy oxygenates when they are photooxidized or react with ozone and NO_3. Their chemistries are quite complex, and their overall effects on the chemistry of the troposphere are not well understood.

Evidence is increasing that the reactions forming organic aerosols may be important in heterogeneous chemistry. Much of the biogenic organic aerosol found in the atmosphere is <0.1 micron in size and therefore might not contribute as much to visibility reduction as sulfate- or nitrate-containing aerosols that are hygroscopic. Because of their larger molecular sizes and therefore significantly lower vapor pressures, the emission rates of monoterpenes are smaller than those of isoprene. With their greater reactivity with ozone as compared to isoprene (see Table 1), monoterpenes may play important roles in removing ozone (Gaffney et al., 1993), particularly at night. Much more research is needed to address the impacts of monoterpenes on regional-and urban-scale chemistries in the troposphere, as well as the effects of pollutant stresses on the emission rates and composition of these trace gases by various plant species.

In conclusion, it is increasingly clear that the biospheric emissions of reactive organic species can play a

Table 1. Calculated half-lives for reactions of propylene and natural hydrocarbons with OH, ozone, and nitrate radical.

Compound	Structure	Half-life			Sources
		OH	O_3	NO_3	
Propylene		10.5 hr	16.5 hr	3 d	Combustion
Isoprene		3 hr	13 hr	1 hr	Deciduous trees
alpha-Pinene		5 hr	2 hr	5.5 min	Conifers
beta-Pinene		3.5 hr	9 hr	13.5 min	Conifers, sage
delta-3-carene		3 hr	1.5 hr	3 min	Gum turpentines
d-Limonene		2 hr	17.5 min	2.5 min	Pine, sage

major role in climate and air quality when the organic species interact with energy-related NO_x and SO_2 emissions in the troposphere. These chemical interactions will affect the gas phase, aerosols, and aqueous phase of the troposphere. As these compounds are oxidized to form highly water soluble species (e.g., formaldehyde) they may also play important roles in the wet deposition and formation of organic peroxides, organic acids, and keto-acids. These species should not be neglected in examinations of the reactions in clouds or in assessments of their roles in the filtering of uv-B radiation. Increased uv-B radiation due to stratsopheric ozone depletion might be filtered by these oxidized organics, since many carbonyl-containing products will absorb radiation in the uv-B window. Thus, studies assessing the effective radiation dosages associated with increases in uv-B on forest ecosystems should take into account pollutant and biospheric gases and associated aerosols.

Acknowledgements

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