The phenomenon of non-linearity refers to the variation of k_S as a result of complex interactions of chemical and physical properties of the atmospheric system. The extent to which k_S varies, as a function of those properties not treated by the modeling systems, is extremely relevant to the credence placed on the linear relationship between SO_2 and SO_4^{2-} formation.

In order that the LRT models account for the formation of HNO_3 and organic acids, they must use similar linear expressions, such as:

$$d[HNO_3]/dt = d[NO_3^-]/dt \tag{4-4}$$

$$= k_N[NO_2 \text{ or } NO_x]$$

$$d[\text{organic acids}]/dt = k_0[\text{hydrocarbons}].$$

4.3 Summary of Possible Acidification Pathways

The major pathways leading to acidification of the air, suspended particles, dews, fog droplets, cloud nuclei, and raindrops are shown in Figure 4.1. Gas-phase photochemical and non-photochemical reactions produce free radicals which may react directly with SO_2, NO_2, and organics to produce acids, or which may react to form long-lived oxidants. Some of the long-lived oxidants may react directly in the gas phase with organics to form organic acids (for example, the O_3-olefin reaction), but they do not react at significant rates with SO_2 and NO_2. Of the long-lived oxidants formed, H_2O_2 is highly soluble, HNO_2 is soluble when pH > 4, O_3 is slightly soluble, and NO_2 is practically insoluble in water. Since SO_2 is also soluble when pH > 3, reactions with dissolved long-lived oxidants could be a major acidification pathway for wet suspended particles, dews, fog droplets, cloud nuclei and raindrops. Also, transition metal ions [especially