

Such a determination can serve as a valuable guide for future experimental studies and for identifying those parameters that, when varied within accepted bounds, will be most influential on the predictions of the mechanism.

Although the qualitative aspects of the chemistry of the polluted troposphere appear to be reasonably well understood, there are many important details that still need to be investigated before a complete quantitative understanding of the photochemical smog system is possible. Several groups (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978) have formulated chemical reaction mechanisms for polluted tropospheric chemistry. Some of these are based on specific surrogate hydrocarbon chemistries; in others, attempts have been made to simulate the complex ambient atmospheric system by representing the general features of the hydrocarbon chemistry. All mechanisms contain aspects of uncertainty, whether in unknown rate constants, in the importance of competing reaction paths, or in the manner of representing the reaction of a generalized species. The measure of the accuracy of a mechanism is usually based on the extent of agreement between predicted concentration profiles and those generated experimentally in smog chambers. But here also, the inherent uncertainty of the experimental data base must be taken into consideration when comparing predictions to observations.

The chemistry of the inorganic portion of the photochemical smog mechanism is, by and large, well understood. Uncertainties remaining include:

- o photolysis rates,
- o alkane-HO product distributions,
- o olefin-HO and olefin-O₃ product distributions,
- o aromatic chemistry,
- o alkoxy radical reactions, and
- o RO_x/NO_x reactions.

Uncertainty in the model prediction can result from inappropriate specification of photolysis rate constants. In the case of computer simulations of smog chamber data, photolysis rate constants relative to the