

## 2.1 *Background for the Examination of Chemical Processes in the Atmosphere*

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### 2.1.1 BACKGROUND PERSPECTIVES

Even relatively clean air contains a large number of highly reactive or toxic compounds such as sulphuric and nitric acids. While life can apparently adapt to small concentrations of atmospheric contaminants, emissions of gaseous and particulate compounds can under certain circumstances begin to harm life on a local and even a global scale. The more obvious detrimental effects of these toxic substances are well documented and range from slight discomfort to serious health problems for man and reduced plant growth to destruction of the ecosystem. The seriousness of this problem was vividly illustrated by the early smog events in London and the more frequent oxidizing smogs experienced in areas like Los Angeles.

Primary emissions include substances that are themselves often toxic, for example sulfur dioxide reduces plant growth and fibrous aerosols such as asbestos may cause lung cancer. In addition, after initial transformation non-toxic emissions such as hydrocarbons often yield toxic oxidants, e.g. hydrogen peroxide, peroxyacylnitrates and carbonyls (formaldehyde) which are known to cause visible damage to plants and can reduce nitrogen fixation thereby affecting natural plant communities and altering fertilizer needs for agricultural crops. The oxidation of sulfur dioxide and of nitric oxide

produces sulfuric and nitric acids, which are deposited as low pH rain water, commonly called acid rain, or as dry fallout of these compounds from large industrial sources. The severity of damage to forests and aquatic life from acid deposition is currently being assessed in many parts of the world in various ways. The cost to the consumer from agricultural losses are of the order of half a billion dollars per year in the United States alone. Corrosion to buildings and metal constructions together with ozone damage to paint, elastomers and textile fiber dye systems is estimated to be several billion dollars per year. The considerable cost from the increase in the frequency of respiratory and pulmonary maladies can be evaluated in terms of the increased burden upon social medicine (Büchel, 1983). Besides these obvious economic and social costs there exists a number of slow changes in atmospheric composition which are difficult to detect and which could be particularly dangerous if allowed to accumulate over a long time period. For example the stratospheric ozone content has been varied by anthropogenic chlorine emission (Hudson and Reed, 1979) and the earth's climate may possibly be affected by the increased carbon dioxide content of the atmosphere (Research Report 104 02 606, 1981). These last examples are especially alarming since the processes may be irreversible for several thousand years.

The adverse effects from air pollutants can be related to the organism's exposure which is the product of concentration and duration. The actual concentration and residence time of air constituents is controlled by a large number of reactions and transport processes in the atmosphere, as well as by interactions with the hydrosphere, the biosphere, and the geosphere (Junge, 1978).

In order to understand the degradation chemistry of synthetic organic pollutants, the general atmospheric and photochemistry of unpolluted air has to be understood. Extensive progress has been made in our knowledge of atmospheric processes through the combined efforts of (1) laboratory measurements on elementary reactions, (2) field measurements of the quantitative distribution of minor constituents and (3) model calculations based on known chemical reactions and transport mechanisms operative in the atmosphere. The present state of our knowledge of chemistry of the atmosphere is presented in Section 2.2.

Many chemicals with high vapour pressures can be degraded in homogeneous gas phase reactions either by photolysis or through attack by reactive chemical species. The relatively advanced laboratory studies of homogeneous gas phase reactions are discussed in Section 2.3 with respect to methodology and the reliability of results. The degradation of chemicals by homogeneous reactions in liquids and by heterogeneous processes on atmospheric aerosols or on the earth's surface are not yet fully described. Large fractions of chemicals with low vapour pressures can be degraded in

the adsorbed state through their excitation by light. Laboratory methodologies related to photochemical degradation are presented and discussed in Section 2.4.

Governmental bodies, faced with the increasing environmental awareness of public, have demanded that manufacturers provide reliable information on the physico-chemical properties, toxicity, ecotoxicity and persistence of the growing number of newly marketed chemicals. For those chemicals which are released into the atmosphere or are otherwise airborne, prediction of harmful environmental impacts requires an initial step test-procedure that allows dependable estimates of the atmospheric degradation rates. The currently used methodologies are evaluated in Section 2.5.

### 2.1.2 REFERENCES

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