

to explain the observed induction time for smog chemistry, but the concentrations necessary to initiate smog chemistry in the atmosphere are below the limits measured by most modern instruments.

Another important source of radicals in the atmosphere is the photolysis of aldehydes:

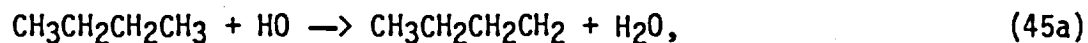


Aldehydes are emitted from many sources, including automobiles. They are also formed by the reaction of ozone with olefins and through reaction 42.

During the course of the overall smog formation process, the free radical pool is maintained by several sources, but the dominant one appears to be photolysis of the aldehydes formed from the initial hydrocarbons. Since the reactions of free radicals with NO form a cyclic process, any additional source of radicals will add to the pool and increase the cycle rate. Conversely, any reaction that removes free radicals will slow the cycle rate. For example, a primary radical sink and a primary sink for oxides of nitrogen is reaction 38 to form nitric acid.

The hydrocarbon classes important in the chemistry of the polluted troposphere are alkanes, alkenes, and aromatics. In addition, the oxygenated hydrocarbons, such as aldehydes, ketones, esters, ethers, and alcohols are also important. A great variety of chemical reactions take place among these organic species and the free radicals cited above. The reactions of typical hydrocarbon species are now discussed briefly. Throughout the discussion, references to more extensive coverages are given.

The most important atmospheric reaction involving alkanes is with the HO radical. For n-butane, for example, the reaction is



and

