

Aldehydes, both aliphatic and aromatic, occur as primary and secondary pollutants and are direct precursors of free radicals in the atmosphere (Lloyd, 1978). Consequently, aldehyde chemistry represents an important subject area in atmospheric chemistry. Although aldehydes are the main oxygenated hydrocarbons generally considered with respect to their role in atmospheric chemistry, other classes of oxygenated hydrocarbons, such as ketones, esters, ethers and alcohols, are present and participate to a somewhat lesser extent. Major secondary sources of aldehydes include the reactions of ozone and OH radicals with hydrocarbons, and radical decomposition products. In addition, aromatic aldehydes can be formed as an ultimate consequence of the reaction of OH with aromatics, e.g., benzaldehyde. The aldehydic hydrogen-carbon bond in aldehydes is relatively weak (CH bond strength is 86 kcal mol⁻¹). Consequently, this hydrogen atom will be susceptible under atmospheric conditions to attack by radical species, such as O(³P), O(¹D), HO, and HO₂. Of these HO is by far the most dominant. Hydroxyl radicals are generally thought to abstract an H-atom from aldehydes-- chiefly the aldehydic H-atoms, i.e.,



If one assumes an atmospheric concentration of 10⁶ HO radicals cm⁻³, the rates of decay of HCHO and CH₃CHO by reaction with OH are approximately 4.2% and 5.8% h⁻¹, respectively (Lloyd, 1978).

The photodissociation of aldehydes is an important radical generation mechanism in the formation of photochemical air pollution. The reactions that are most significant can be generalized in terms of a radical and a molecular route:



and

