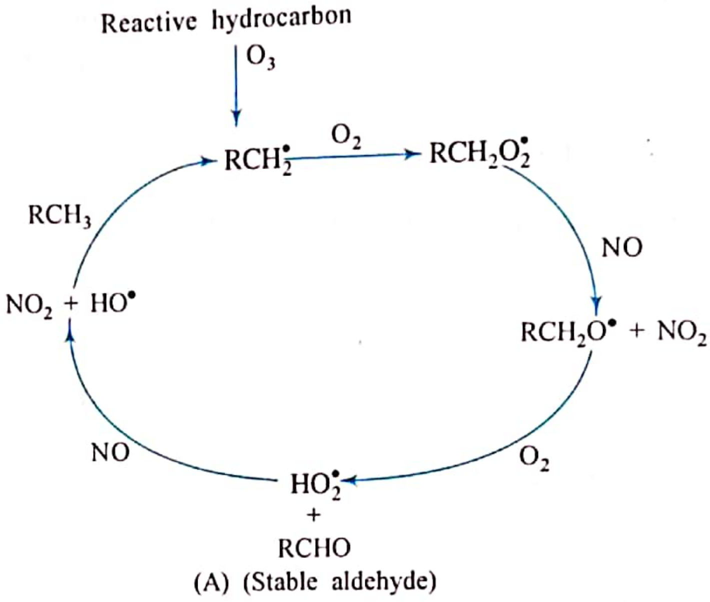
or water-soluble products, e.g., acids and aldehydes,

Photochemical Smog

Majority of the harmful effects of hydrocarbon pollution are not due to the hydrocarbons themselves but the products of photochemical reactions in which they are involved. Hydrocarbons do not react readily with sunlight, but they are reactive towards other substances produced photochemically. An important characteristic of atmosphere which is loaded with large quantities of automobile exhausts, trapped by an inversion layer (stagnant air masses) and at the same time exposed to intense sunlight, is the formation of photochemical oxidants in the atmosphere. This gives rise to the phenomenon of *photochemical smog* which is observed in localities like Los Angeles and Denver, USA. It may be mentioned that 'smog' originally means an odd combination of smoke and fog prevalent in London. This is, however, chemically reducing with high levels of SO_2 (see Sec. on SO_2) and is called *reducing smog*, whereas *photochemical smog* is an *oxidising* smog having a high concentration of oxidants. Photochemical smog is characterised by brown, hazy fumes which irritates the eyes and lungs, and also leads to the cracking of rubber and extensive damage of plant life.

The probable mechanism of smog-forming reactions is illustrated in the flow charts (Fig. 10.6 A, B):



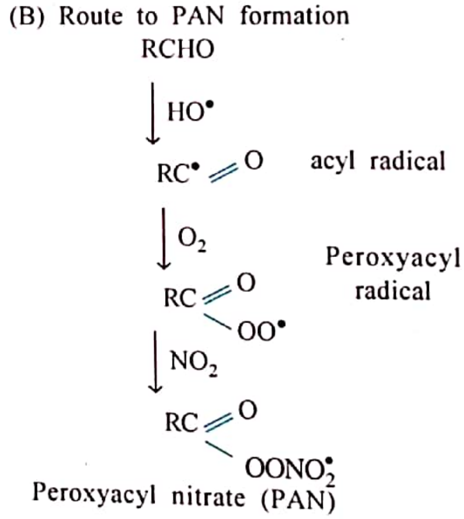


Fig. 10.6(A) Smog-formation reactions (B) PAN formation reactions

(*i*) Reactive hydrocarbons (those with C = C groups) from auto-exhaust interact with O_3 to form a hydrocarbon-free radical $RCH_2^{\bullet}$.

(*ii*) $RCH_2^{\bullet}$ rapidly reacts with O_2 to form another free radical $RCH_2O_2^{\bullet}$.

(*iii*) $RCH_2O_2^{\bullet}$ reacts with NO to produce NO_2 and the free radical $RCH_2O^{\bullet}$.

(*iv*) This new free radical next interacts with O_2 to yield a stable aldehyde, RCHO, and hydroperoxyl radical $HO_2^{\bullet}$.

(*v*) $HO_2^{\bullet}$ then reacts with another molecule of NO to give NO_2 and $HO^{\bullet}$.

(*vi*) $HO^{\bullet}$ is extremely reactive and rapidly reacts with a stable hydrocarbon RCH_3 to yield H_2O and regenerate the hydrocarbon-free radical $RCH_2^{\bullet}$, thereby completing cycle. This goes on and on as a chain reaction. One complete cycle yields two molecules of NO_2, one molecule of aldehyde RCHO, and regenerates the free radical $RCH_2^{\bullet}$ to start all over again. Very soon there is a rapid build-up of smog products.

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(*vii*) The aldehyde RCHO may initiate another route by interaction with the HO$^{\cdot}$ radical, leading to the formation of an acyl radical RC=O, peroxyacyl radical $RCOO_2^{\cdot}$ (by reaction with O_2), and finally peroxyacyl nitrate, PAN (by reaction with NO_2). PAN is one of the most potent eye irritants found in smog.

Photochemical smog shows characteristic variation of the parameters (smog ingredients) with the time of day. The hydrocarbon level is maximum during early morning traffic rush hours, then decreases during the remaining daylight hours as it is consumed in the smog-formation reactions described above. Nitric oxide concentration has a peak value at the same time and then falls as NO_2 concentration increases. Subsequently, there is a rise in the concentration of oxidants (aldehyde, PAN), which are active oxidising agents and contain the irritating ingredients of smog. A typical concentration profile of smog-forming chemicals in Los Angeles air in USA is shown in Fig. 10.7.

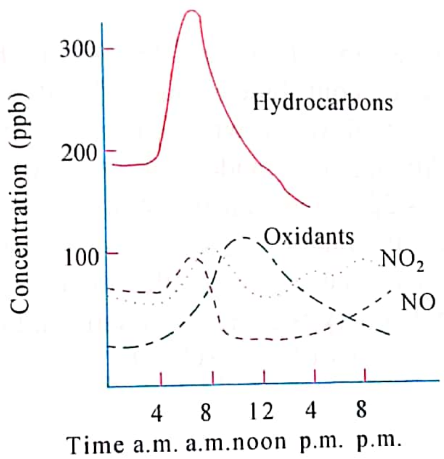

Fig. 10.7 Concentration profiles of smog-forming chemical in Los Angeles air (*Source:* J.A. Kerr, J.G. Calvert and K.L. Demerjian, *Chem. B.*, 8(1971): p. 253.)