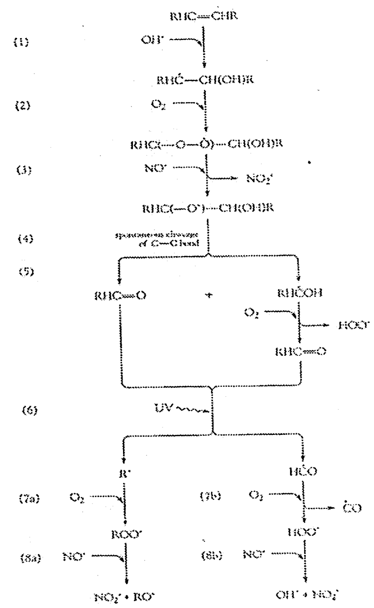
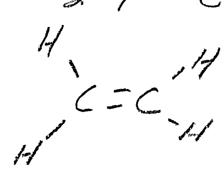
FIGURE 3-10 Mechanism of the RHC═CHR reaction in photochemical smog.

Decomposition of VOC's

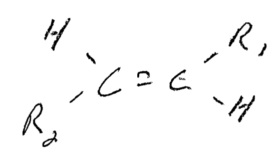


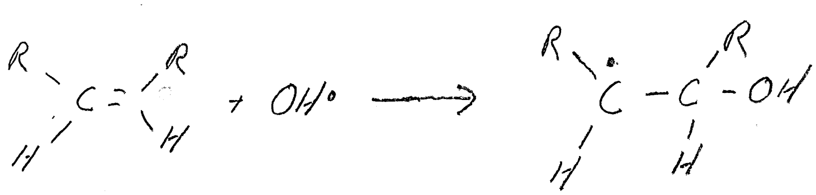
Oxidation of hydrocarbons
many VOC's have reactive (C=C)

Examp. C_2H_4 ethylene

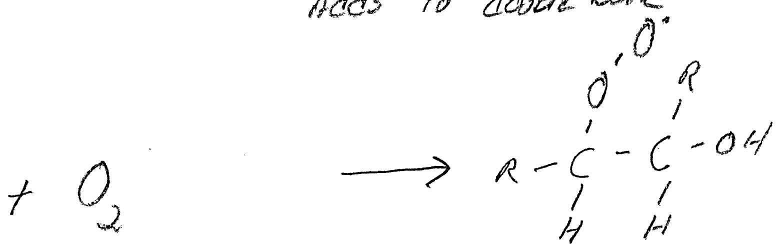


or

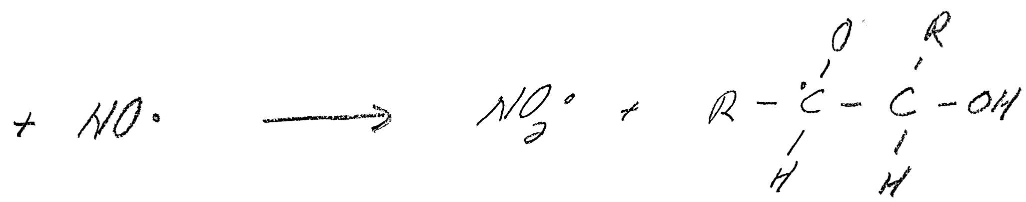




adds to double bond



oxygen adds to form peroxy radical



peroxy radical oxidizes $NO\cdot$ to $NO_2\cdot$

After $NO\cdot$ has been conerted to $NO_2\cdot$

$$NO_2\cdot \xrightarrow{\lambda < 400nm} NO\cdot + O$$

only sign. source of atomic oxygen in trop.

$$O + O_2 \rightarrow O_3$$

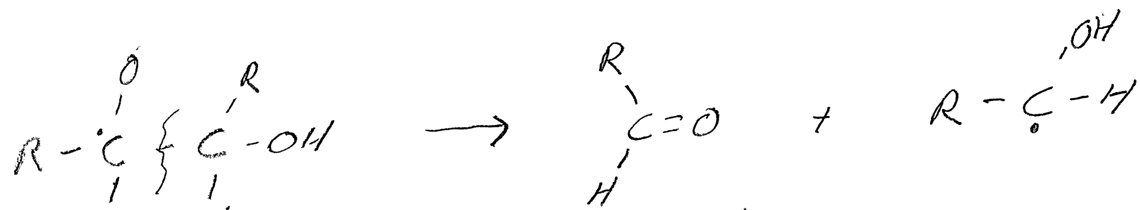
Since

$$NO\cdot + O_3 \rightarrow NO_2\cdot + O_2$$

nullifing previous two rxns

O_3 does not build up until peroxy radicals convert most $NO\cdot$ to $NO_2\cdot$

<u>Back to hydrocarbon radical</u>



aldehyde

Rxn requires almost no energy (ΔH is close to zero and E_a is very small

formation of C=O compensates for breaking C-C bond

$$R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}\cdot + O_2 \longrightarrow HOO\cdot + \underset{H}{\overset{R}{}}C=O$$

aldehyde

$$\xrightarrow{h\nu} R\cdot + HCO\cdot$$

produces a large increase in free radical concentration (relative to normal)

Fate of Free Radicals

In the later stages of smog events (free rad. build up)

$$OH\cdot + NO_2\cdot \longrightarrow HNO_3$$

two radicals generally form a stable non-radical product

(primary trop. sink for OH·)

In polluted areas

$$OH\cdot + NO\cdot \longrightarrow HONO \xrightarrow{h\nu} OH\cdot + NO\cdot$$

night — morning

leads to diurnal variations (big influx of radical for the ox. of VOC's)

Later stages of smog events

$$OH^\circ + OH^\circ \rightarrow H_2O_2$$

$$OOH^\circ + OOH^\circ \rightarrow H_2O_2 + O_2$$

hydrogen peroxide

$$R-C(=O)-H + OH^\circ \rightarrow R-\overset{O}{\overset{\|}{C}}\cdot + H_2O$$

$$\downarrow O_2$$

$$R-C(=O)-O-O\cdot$$

$$\downarrow NO_2^\circ$$

for $R = CH_3$

$$R-C(=O)-O-O-NO_2$$

peroxyacetylnitrate
PAN

Oxidizing Agents

$$O_3,\ H_2O_2,\ HNO_3,\ PAN$$