

# 8<sup>th</sup> European Chemistry Congress

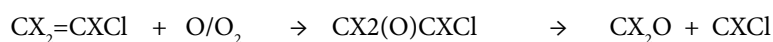
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## Halocarbenes may deplete atmospheric ozone

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Carbenes are formed in gas phase photooxidations of halogenated ethylenes (HEs). In the case of simulated tropospheric photooxidation smog chamber studies of tetrachloroethylene (PERC) and trichloroethylene (TCE), the formation of di- and trichloroacetyl chloride, and the accelerated simultaneous decreasing ozone/PERC and ozone/TCE concentrations along with increasing  $\text{CCl}_2\text{O}$  after a time delay can be best explained by the presence of  $\text{CCl}_2$  in the case of PERC and  $\text{CCl}_2$  or  $\text{CHCl}$  carbene in the case of TCE. The carbene, chlorinated acetyl chloride and  $\text{CCl}_2\text{O}$  products may all result from the rearrangement of the corresponding oxidized/excited oxidized HE intermediate, e.g., an epoxide ( $\text{X} = \text{H, Cl, F}$ ),



New analyses indicate i) halocarbenes may form complexes with  $\text{O}_3$  which can lead to dissociation of  $\text{O}_3$  to  $\text{O}_2$  and  $\text{O}$  and regeneration of carbene resulting in a chain reaction ii) the accelerated  $\text{O}_3$  depletion is not due to  $\text{Cl}$  atoms being photolyzed from reactant chlorinated ethylenes since they do not absorb UV light above 280 nm which is the shortest wavelength light used in the systems iii) scavenging experiments have not proved the existence of  $\text{Cl}$  atoms iv) the need to consider the possibility of the world-wide used perhalocarbons, e.g., PFCs, hydroperhalocarbons, their halogenated replacements and starting materials degrading to halocarbenes which may react with ozone.

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