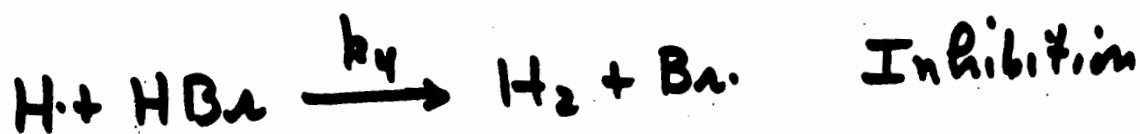
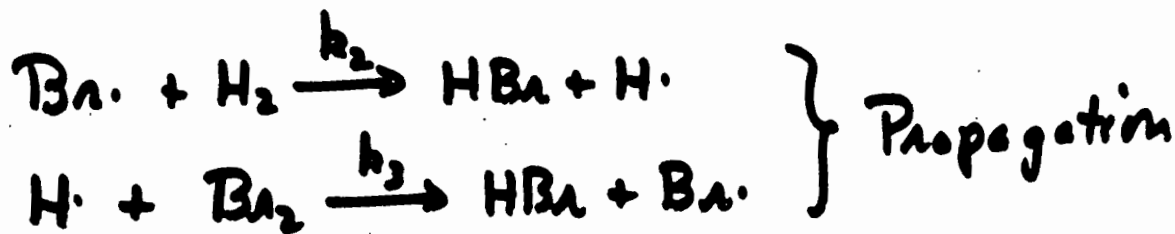
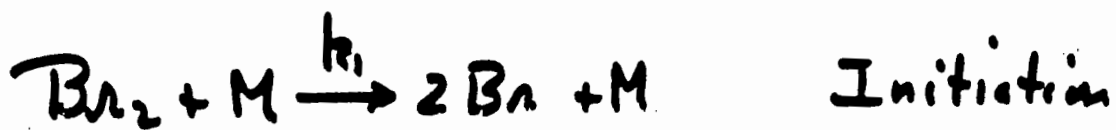


Proposed Mechanism of $H_2 - Br_2$ Reaction.

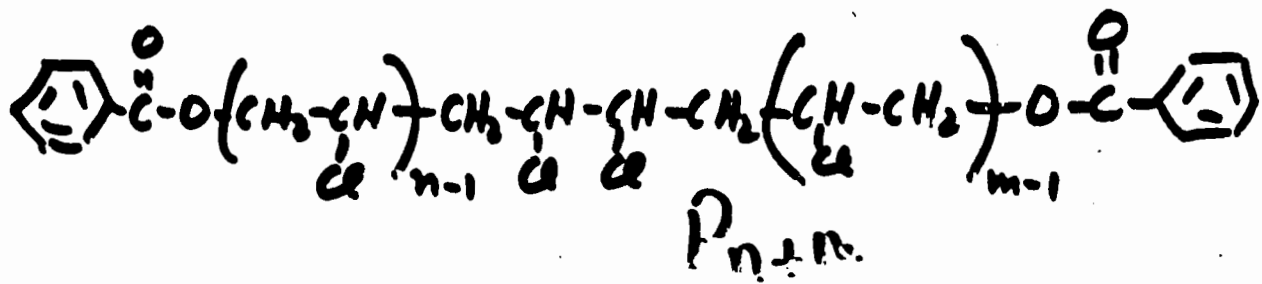
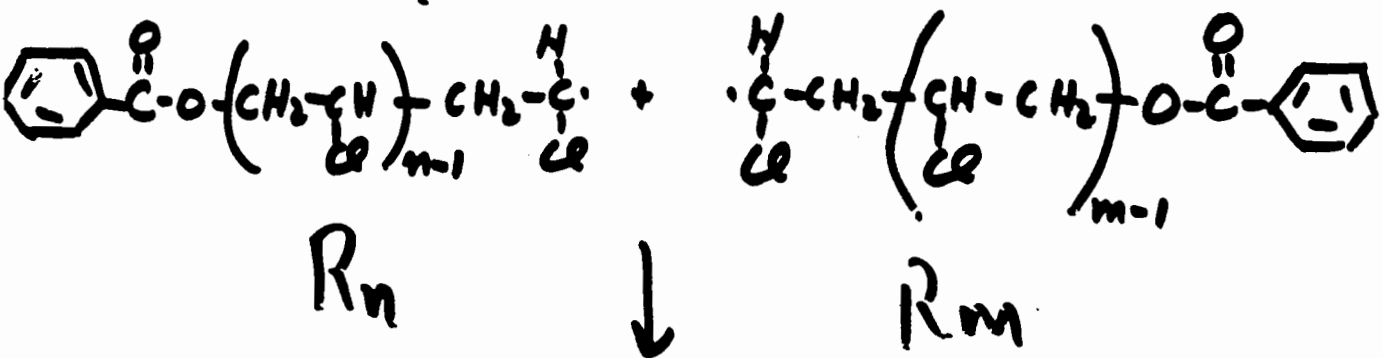
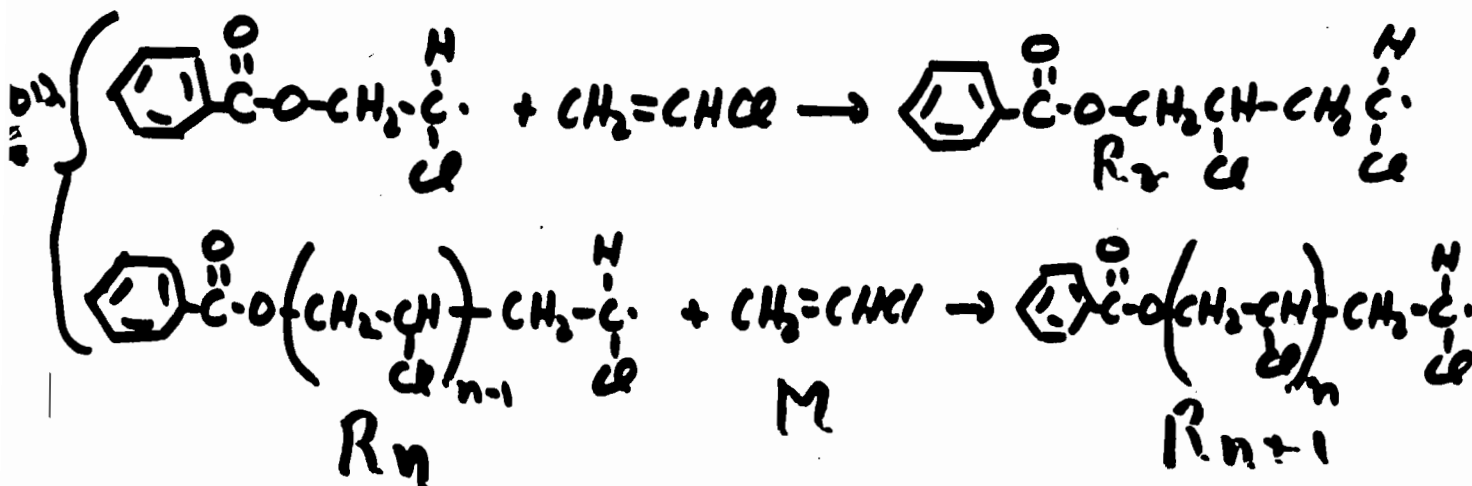
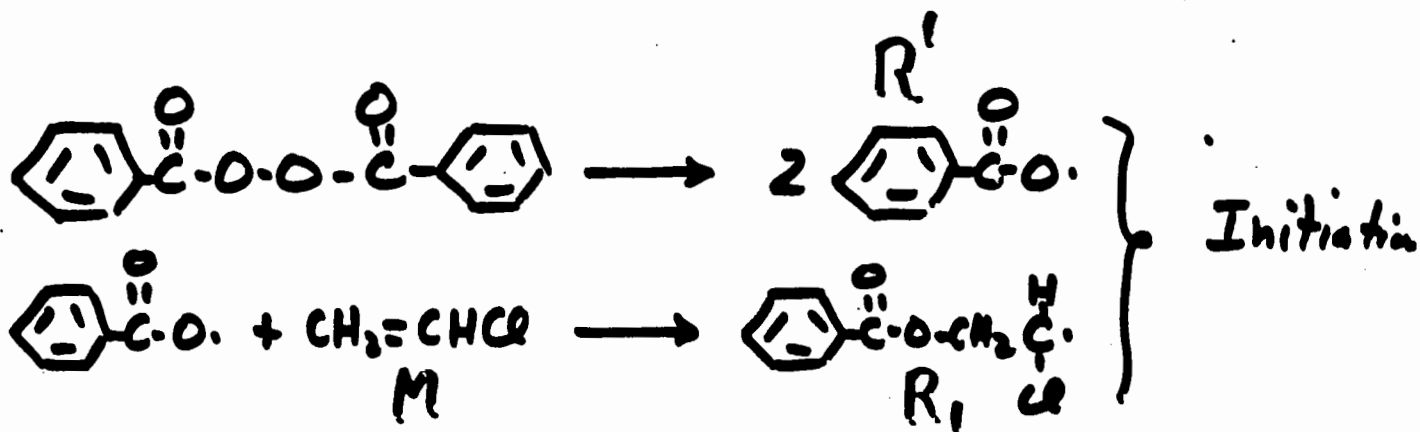


Experimental studies have shown that the rate law is:

$$-\frac{d[H_2]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

Example - Polymerization of Vinyl Chloride

I = dibenzoyl peroxide



Free Radical Chain Polymerization

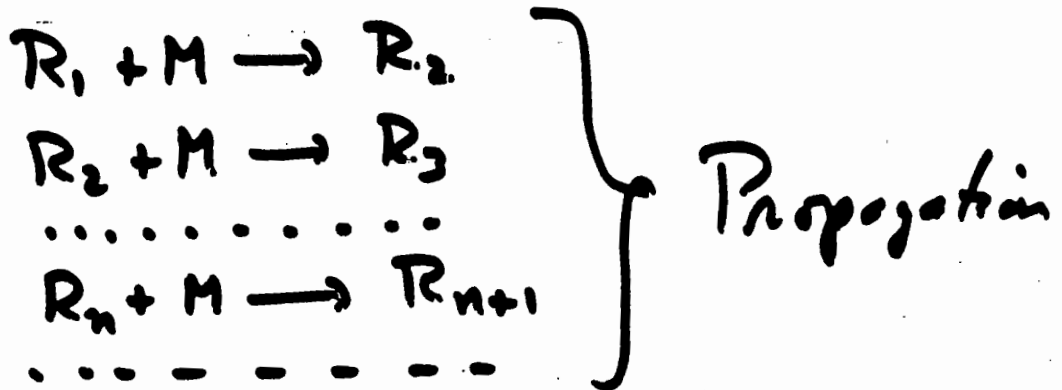
Let I : Initiator

M : monomer

P_n : polymer containing n -monomers

R' : initiating radical

R_i : propagating radical containing i monomer molecules

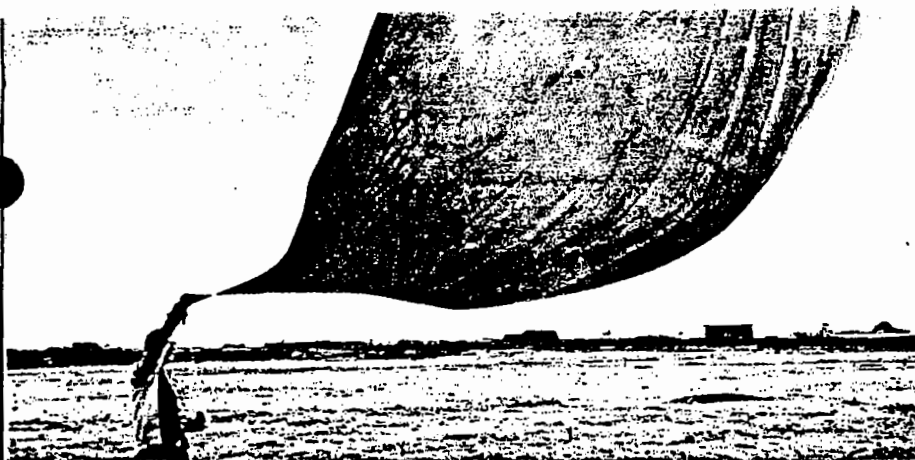


$\chi \equiv$ Kinetic Chain Length

$$\chi = \frac{\text{rate of propagation}}{\text{initiation rate}}$$

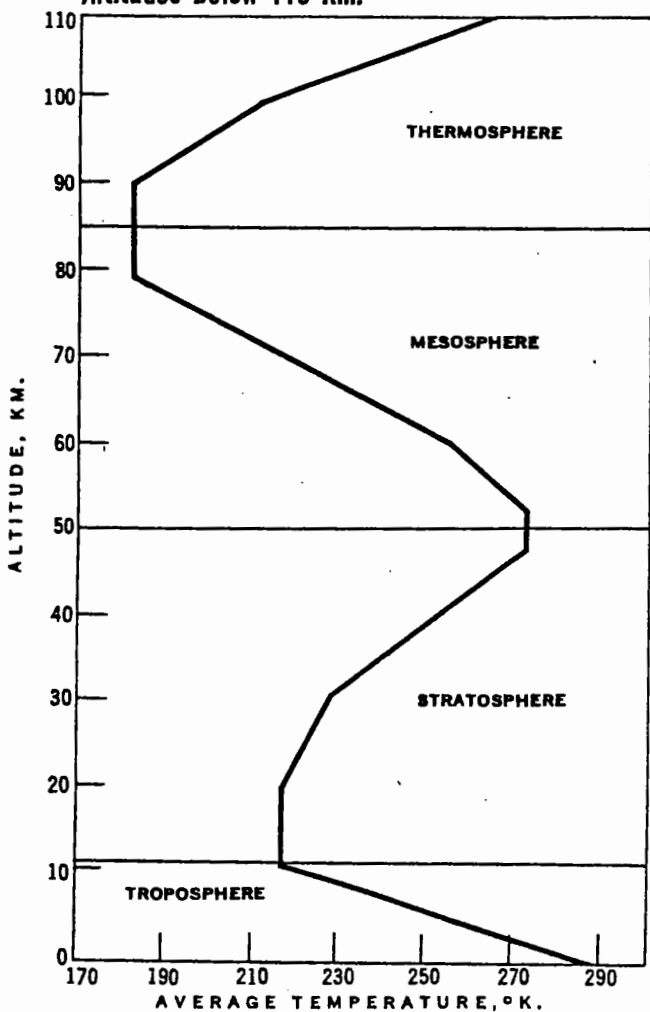
Long Ave. Polymer
Length \Rightarrow

- when termination steps are slow, then propagation steps
- lower rate of initiation.



A technician prepares to release a neoprene balloon that will carry an instrument aloft to measure the vertical distribution of ozone in the stratosphere. Information will also be obtained on atmospheric pressure, temperature, and humidity

Temperature Variations in the Atmosphere at Altitudes Below 110 Km.



Source: "U.S. Standard Atmosphere, 1962," U.S. Government Printing Office, Washington, D.C., 1962.

death of Queen heard at Oxford away but not a closer.

Not until about discover the real that the sound back to the earth tively high temperature. Because through warm air warm air tends waves back to t fractured waves stri points but not at to the source.

Ozone in the Stratosphere

The stratosphere, has essentially the same composition. What is very significant is the presence of ozone, although the concentration of ozone is extremely low, about 0.04 p.p.m. in the maximum of about 25 km altitude of about 25 km in the stratosphere. The ozone content of the atmosphere is indicated by the fact that if the ozone were brought down to earth's surface and standard conditions of pressure, it would form a layer about 0.3 cm. thick.

Although only a small amount of ozone exerts a protective effect on the atmosphere and absorbs the sun's ultraviolet rays from 2100 to 2900 Å, if these rays were not removed, life on earth would be impossible. Many forms of life exist.

By absorbing ultraviolet rays, ozone causes heating of the stratosphere. This helps maintain the heat balance of the atmosphere.

The first quantitative measurements of the amount of ozone in the atmosphere were made by the French chemist, Charles Fabry in 1906. Originally, the gas itself was identified in the air near the ground by Prof. Christian Doppler, a German-Swiss chemist, in 1840. In 1930, Dr. Chapman, a British physicist, first suggested that ozone was

TABLE 1.2 TYPICAL CONSTITUENTS OF AIR IN THE TROPOSPHERE

Species	Typical Mole Fraction*
H ₂ O	10 ⁻⁵ -10 ⁻²
Ne	1.82 × 10 ⁻⁵
CH ₄	1.5 × 10 ⁻⁶
Kr	1.14 × 10 ⁻⁶
O ₃	10 ⁻⁸
N ₂ O	2 × 10 ⁻⁷
H ₂	5 × 10 ⁻⁷
CO	6 × 10 ⁻⁸ -2 × 10 ⁻⁷
Xe	8.7 × 10 ⁻⁸
NO + NO ₂	5 × 10 ⁻¹⁰ -2 × 10 ⁻⁸

* Mole fraction = mixing ratio, or 'volume mixing ratio'; chemists generally prefer the former term, physicists the latter.

length δz . Hence

$$-\delta P = \delta z \cdot \rho \cdot g$$

or in the limit $\delta z \rightarrow 0$

$$dP/dz = -\rho g \tag{1.5}$$

where g is the acceleration due to gravity and ρ is the gas density. For air we can use the perfect gas equation

$$PV = nRT \tag{1.6}$$

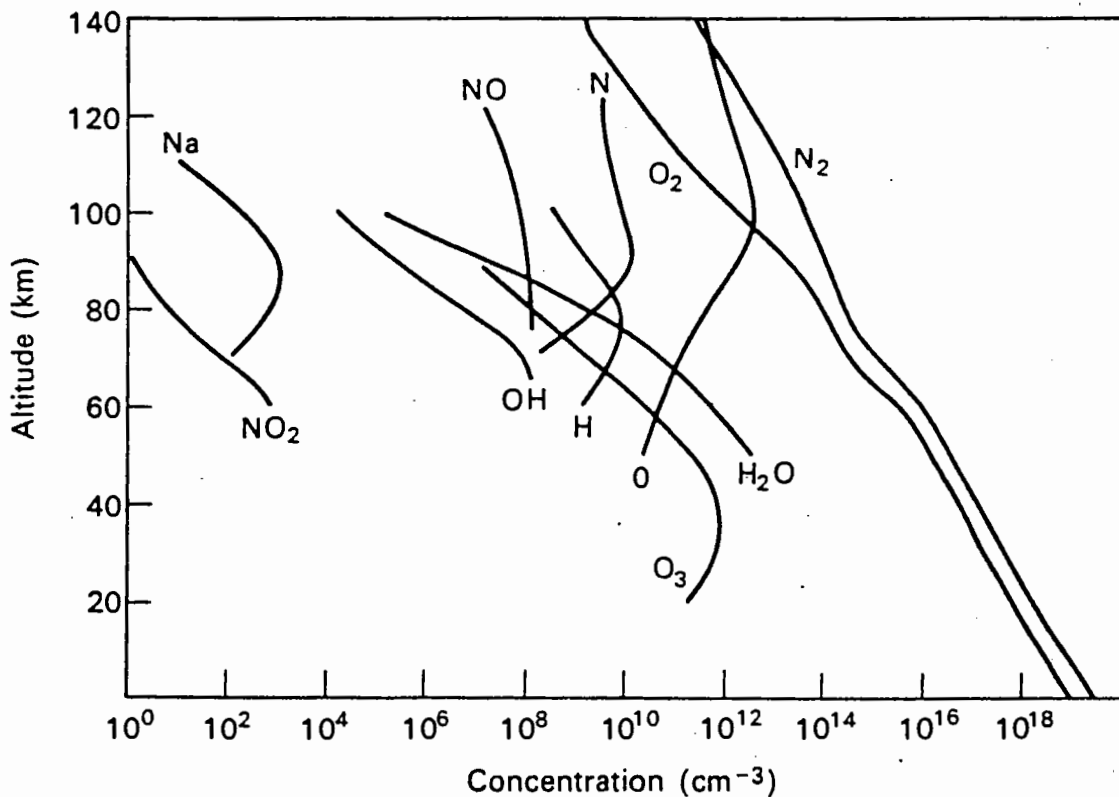


Fig. 1.2 Representative concentration profiles of neutral species in the atmosphere.

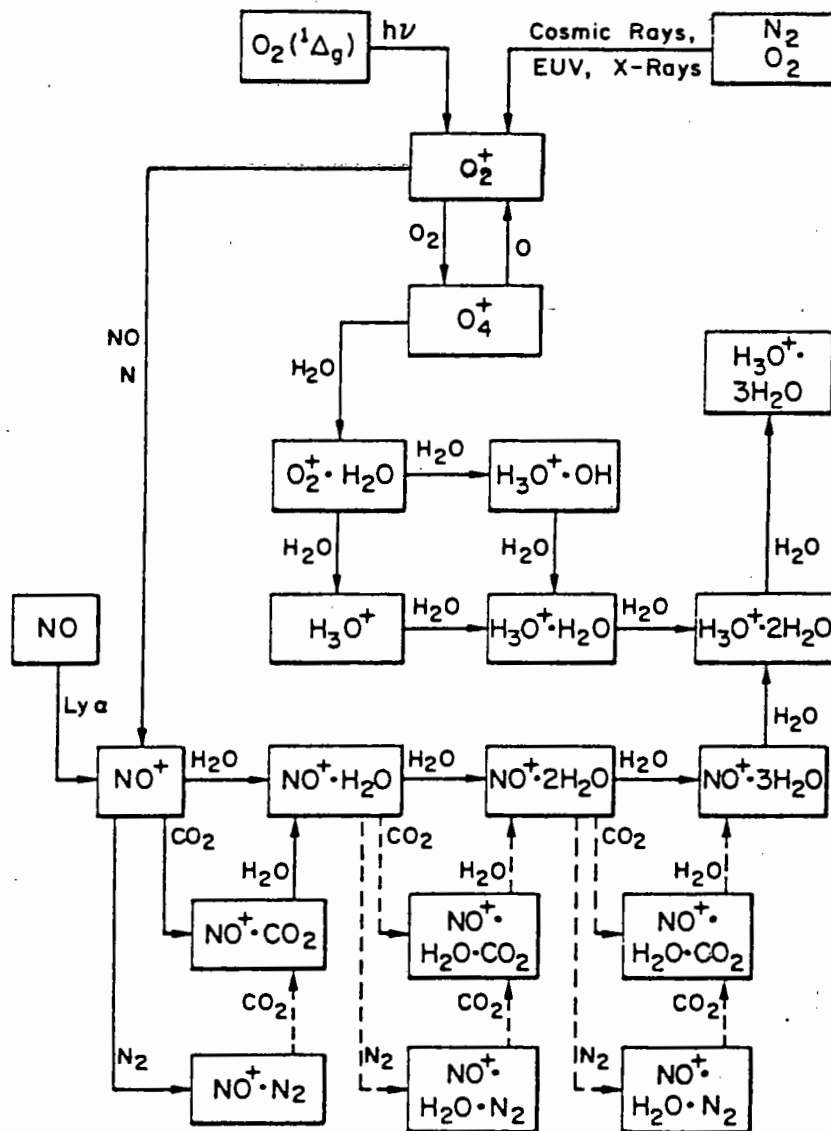
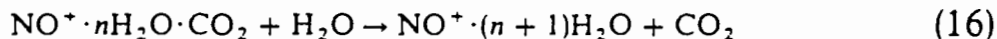
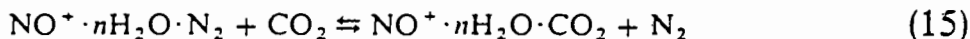


FIG. 7 D-region positive ion chemistry.

where $n = 0, 1, 2$ and $X = N_2, CO_2$. The weakly bound association complexes thus formed would then undergo a series of fast switching reactions,



that would greatly accelerate each hydration step and hence the eventual production of the water cluster ions. These reaction paths are shown in the lower part of Fig. 7. However, the verification of this scheme in the laboratory or the detection of the key ions in the atmosphere has presented a formidable experimental problem, since the intermediate $NO^+ \cdot nH_2O \cdot X$ ions are extremely fragile.

Arnold and Krankowsky (1974, 1977a) have had considerable success in solving the problem of sampling such weakly bound cluster ions in rocket-borne mass spectrometers. As a result, some key ions in this reaction scheme

For this reason, the conversion of NO^+ ions to the observed water cluster ions is extremely sensitive to temperature, and the D-region positive ion composition will, therefore, manifest strong seasonal, latitudinal, and even irregular variations as a result of variations in the atmospheric temperature. Moreover, electron-ion recombination coefficients for these weakly bound cluster ions may be considerably larger than those for the unclustered NO^+ and O_2^+ ions, which may explain, at least in part, the strong variations in the electron density that are observed at about 80 km (Arnold and Krankowsky, 1977a; Reid, 1977). While many of the details still await laboratory verification, the reaction scheme shown in Fig. 7 has been shown (Reid, 1977) to qualitatively solve the long-standing D-region problem of the conversion of the primary NO^+ ions into the observed water cluster ions.

IV. D-REGION NEGATIVE ION CHEMISTRY

In contrast to the D-region positive ion chemistry, where *in situ* measurements discovered the unexpected water cluster ions, the negative ion chemistry of the D-region has been derived predominately from laboratory

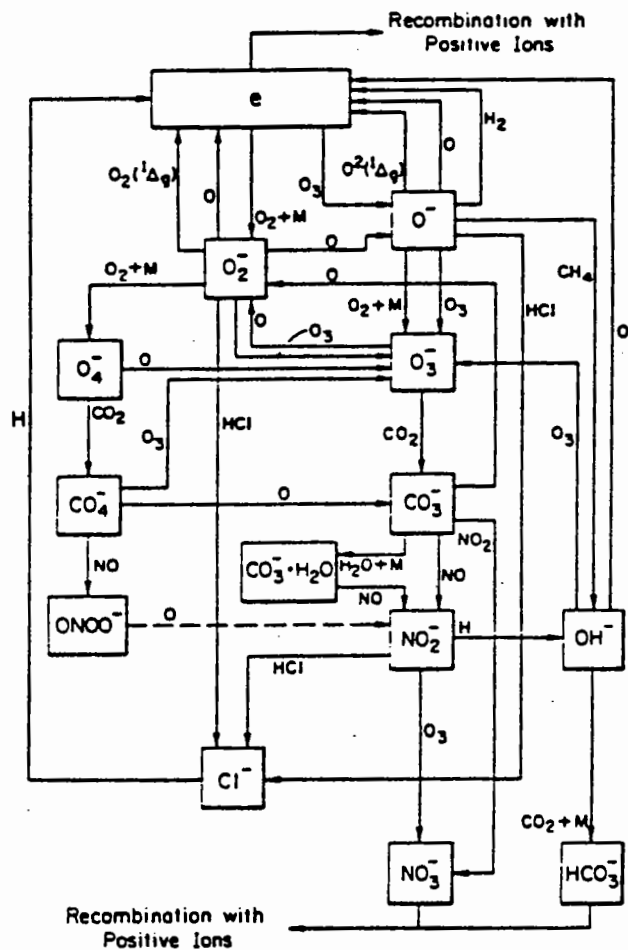


FIG. 9 Reaction scheme for D-region negative ion chemistry.

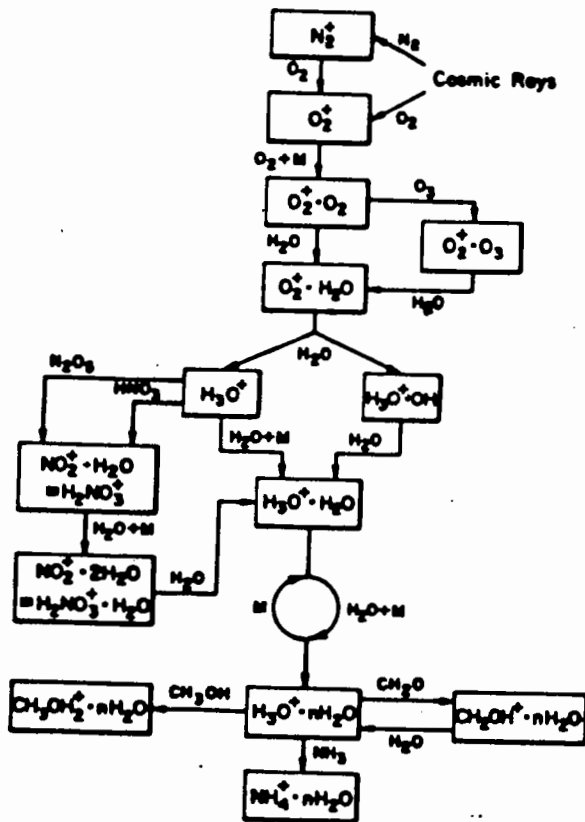


FIG. 13 Stratospheric and tropospheric positive ion chemistry.

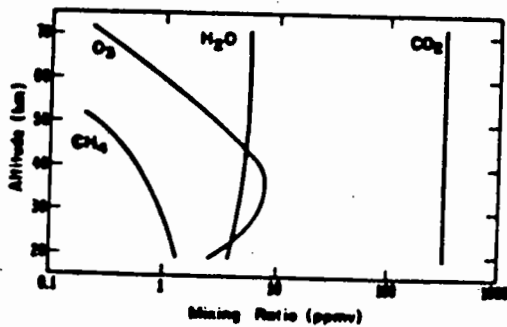


FIG. 14 Mixing ratios of CH_4 , O_3 , H_2O , and CO_2 as a function of altitude. [From Dotan et al. (1978b).] The concentration of CH_4 is from Crutzen et al. (1978) and those of O_3 , H_2O , and CO_2 are from Dubin et al. (1976).

2. ION CHEMISTRY OF THE E

$\text{O}_2^+ \cdot \text{O}_2$ Reactions

Reactions
(1) $\text{O}_2^+ \cdot \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{O}_2$
(2) $\text{O}_2^+ \cdot \text{O}_2 + \text{CH}_4 \rightarrow \text{products}$
(3) $\text{O}_2^+ \cdot \text{O}_2 + \text{CO}_2 \rightleftharpoons \text{O}_2^+ \cdot \text{CO}_2 + \text{O}_2$
(4) $\text{O}_2^+ \cdot \text{O}_2 + \text{O}_3 \rightleftharpoons \text{O}_2^+ \cdot \text{O}_3 + \text{O}_2$

* $1.5(-9)$ means 1.5×10^{-9} , etc.

These $\text{O}_2^+ \cdot \text{O}_2$ reactions (1978b) and the results are given against which the alternative reaction of $\text{O}_2^+ \cdot \text{O}_2$ with CH_4 , CO_2 and O_3 were studied in e are given. For CO_2 , the equi O_2 to CO_2 in the atmosphere strongly favor $\text{O}_2^+ \cdot \text{O}_2$ rather the reaction involving O_3 is r ion concentrations will be muc of the $\text{O}_2^+ \cdot \text{O}_3$ and $\text{O}_2^+ \cdot \text{O}_2$ e lated from the atmospheric det chemical data. The $\text{O}_2^+ \cdot \text{O}_3$ i dropping below one-tenth of This means that the $\text{O}_2^+ \cdot \text{O}_3$ <

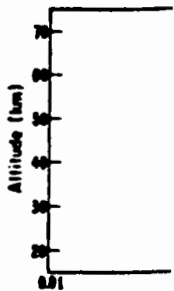


FIG. 15 Calculated equilibrium [From Dotan et al. (1978b).]

The negative ion chemistry of the stratosphere and troposphere is even more speculative than the positive ion chemistry of these regions. In addition to there being few measurements of the trace neutrals involved, there are no negative ion composition data. Furthermore, the D-region measurements, from which one could draw guidance, are relatively sparse and somewhat ambiguous at present, as pointed out in Section IV. Thus, our present understanding of the negative ion processes in the lower atmosphere stems entirely from laboratory studies. [See Notes added in proof, (e).]

The approach here has been to start with the D-region negative ion chemistry given in Fig. 9 and modify it to be in accord with the expected differences in neutral composition of the two regions. These considerations fall into two classes. First, to look for possible alternatives to the chemistry that leads to the NO_3^- ions and second, to consider whether these ions would react with trace neutral species that are suspected in the lower atmosphere to form even more stable ions.

The first necessary modification of the D-region scheme is to disregard the reactions of atomic oxygen, whose concentration below 50 km is negligible in comparison to that of O_3 . In addition, NO will no longer play a role.

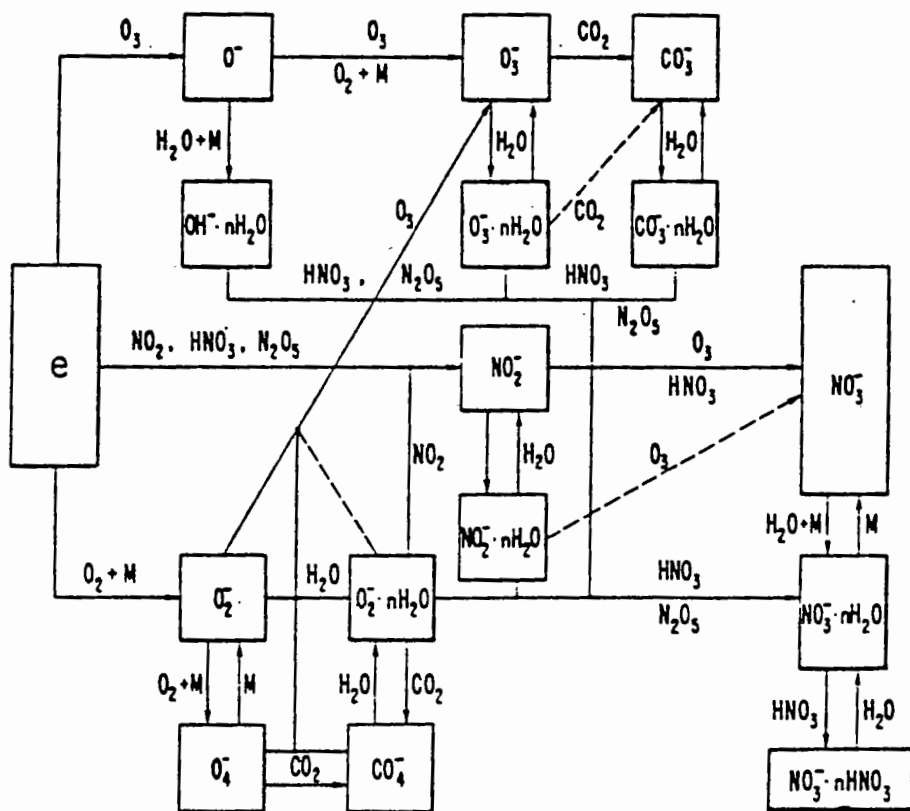
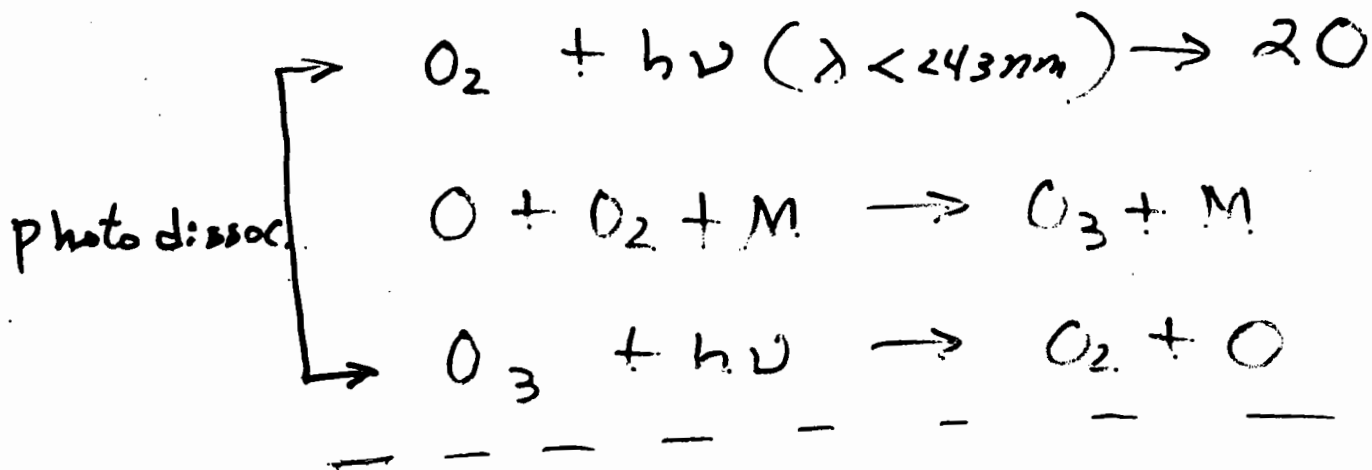


FIG. 17. Stratospheric and tropospheric negative ion chemistry.

Ozone Cycle

Maximum Conc. \sim 25 km elevation

above 20 km :



lower elevations :



Chapman
Mech.



proposed 1930

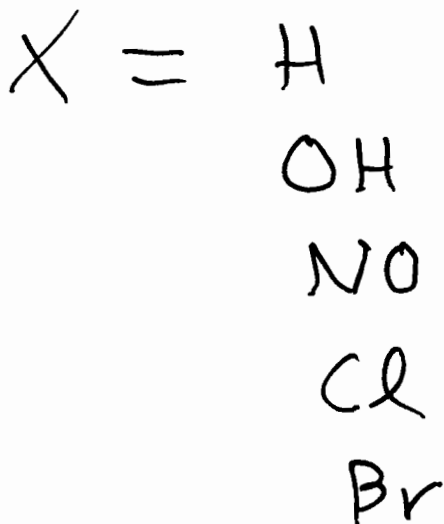
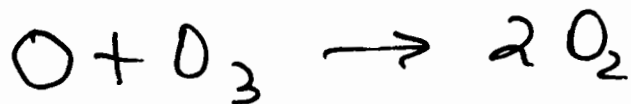
accepted until 1950's

Now Known

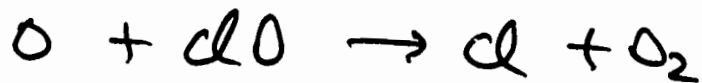
Ozone in the stratosphere - removed
Predominantly by catalytic cycles:



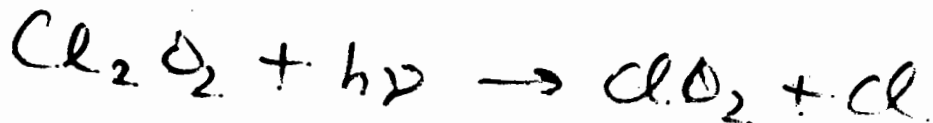
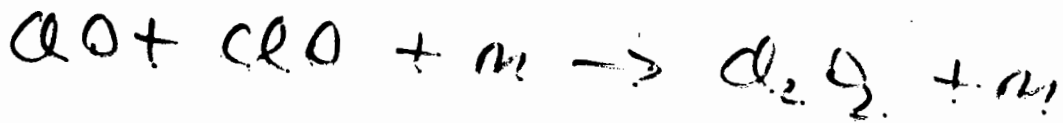
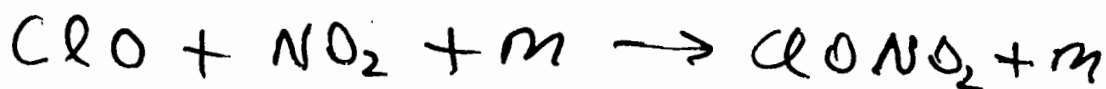
Net:



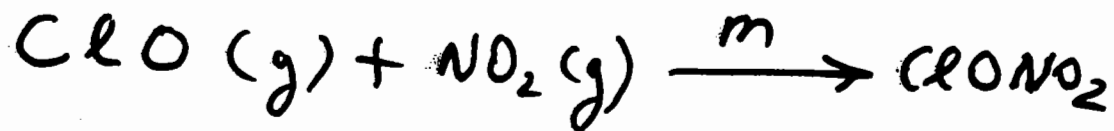
Some other Imp. Mechanisms



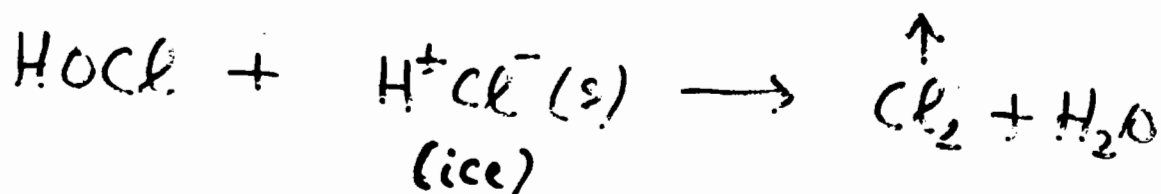
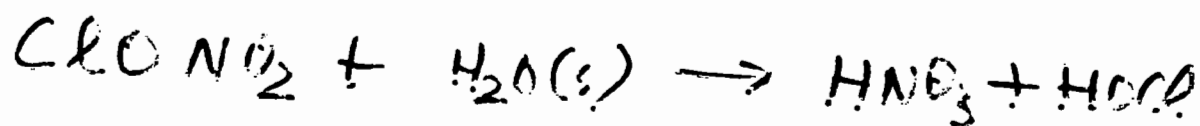
Coupling:



Other Reactions Pertaining to the Ozone Hole Problem



Hydrolysis reactions:



Photochemical Reactions -

Without them the world would be a sterile place

photosynthesis -

Capturing the sun's radiant energy

In the context of last class

$O(^1D)$ produced



Consider Quantum Efficiency

Photochemical Reactions

- molecule absorbs a photon
- Stark - Einstein / each molecule which takes part in photochemical reaction absorbs one quantum of light which induces the reaction (not always valid)
- Law does not imply only one molecule is consumed for each photon absorbed

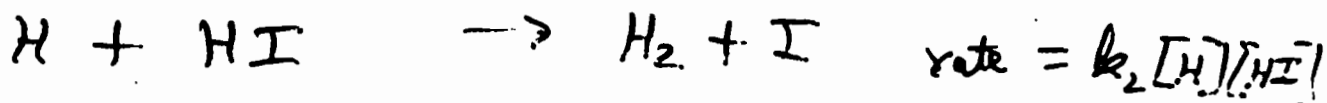
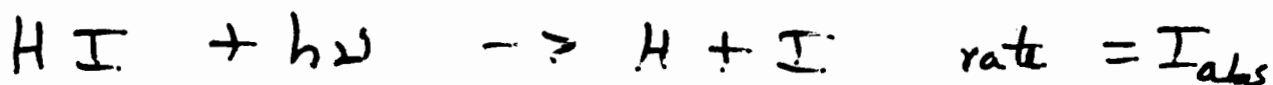
$\Phi \equiv$ quantum efficiency

$$= \frac{\# \text{ reactant molecules destroyed}}{\# \text{ of photons absorbed}}$$

$$\Phi = \frac{-d[I]/dt}{\# \text{ quanta absorbed}} \text{ sec}$$

HI Photochemical dissociation

16



$$-\frac{d[\text{HI}]}{dt} = I_{\text{abs}} + k_2 [\text{H}][\text{HI}]$$

$$\frac{d[\text{H}]}{dt} = I_{\text{abs}} - k_2 [\text{H}][\text{HI}] = 0$$

Steady-state

$$\therefore k_2 [\text{H}][\text{HI}] = I_{\text{abs}}$$

$$\therefore -\frac{d[\text{HI}]}{dt} = I_{\text{abs}} + I_{\text{abs}}$$

$$\Phi = \frac{2 I_{\text{abs}}}{I_{\text{abs}}} = 2$$