THE EFFECT OF PARTICLE PRECIPITATION EVENTS ON THE NEUTRAL AND ION-CHEMISTRY OF THE MIDDLE ATMOSPHERE: II. ODD HYDROGEN

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Abstract—A one dimensional time-dependent model of the neutral and ion chemistry of the middle atmosphere has been used to examine the production of odd hydrogen (H, OH, and HO_2) during charged particle precipitation. At altitudes above about 65 km, odd hydrogen production depends on the ionization rate, and the atomic oxygen and water vapor densities. Odd hydrogen production is shown to exhibit diurnal and other time dependent variations during such an event at these altitudes, and the assumption that two odd hydrogen particles are always produced per ionization is reexamined.

INTRODUCTION

The production of odd hydrogen (H, OH) during charged particle precipitation events is believed to result in decreased ozone concentration in the mesosphere and upper stratosphere. This effect was first suggested by Swider and Keneshea (1973) in an attempt to explain rocket observations of ozone during the 2 November 1969 PCA obtained by Weeks *et al.* (1972). In order to evaluate the impact of the injected odd hydrogen on atmospheric ozone, however, it is necessary to consider how many odd hydrogen particles are produced per ionization. Most previous studies dealing with ozone chemistry have not calculated this production explicitly, but have instead assumed that two odd hydrogen particles are always produced per ionization (e.g. Crutzen and Solomon, 1980; Swider *et al.*, 1978). On the other hand, studies of atmospheric ion chemistry have pointed out that odd hydrogen production depends on such factors as the atomic oxygen density (Fehsenfeld and Ferguson, 1972) and the electron density (Reid, 1972; Reid, 1976). The possibility that odd hydrogen production could depend on the ion chemistry was suggested previously by Frederick (1976). In this study we examine the feedbacks between the ion and neutral chemical composition during a particle precipitation event. We consider the time, altitude, and diurnal variations in species such as atomic oxygen, for example, and their effect on the number of odd hydrogen particles produced per ionization as the event proceeds.

Using the 2 November 1969 solar proton event (SPE) as an example, we discuss the impact of the odd hydrogen produced by the event on atmospheric ozone.

CHEMISTRY OF ODD HYDROGEN PRODUCTION

The flow of positive charge following ionization is schematically illustrated in Fig. 1. It should be emphasized that many of the chemical processes under discussion here, particularly for the ions, are quite uncertain. However, using the currently accepted chemistry we wish to indicate what factors may possibly influence odd hydrogen production during particle precipitation events. The relative production of O_2^+, N_2^+, O^+, and N^+ is a result of the abundances of O_2 and N_2 and the ratios of their dissociative ionization and ionization cross-sections as described by Rusch *et al.* (1980). Thus, for example, the rate of production of N^+ is 18.5% of the total ionization rate. In the *D*-region, most of the N_2^+, N^+, and O^+ charge exchanges to form O_2^+, but a portion of the N^+ and O^+ may react to form NO^+ as shown. The formation of NO^+ is a potential source of odd hydrogen, and is believed to be responsible for the formation of oxonium ions in the quiet *D*-region (Reid, 1977). During disturbed conditions at high altitudes, however, electron concentrations are expected to be relatively high, and the intermediate ions such as $NO^+ \cdot CO_2$ may recombine before odd hydrogen

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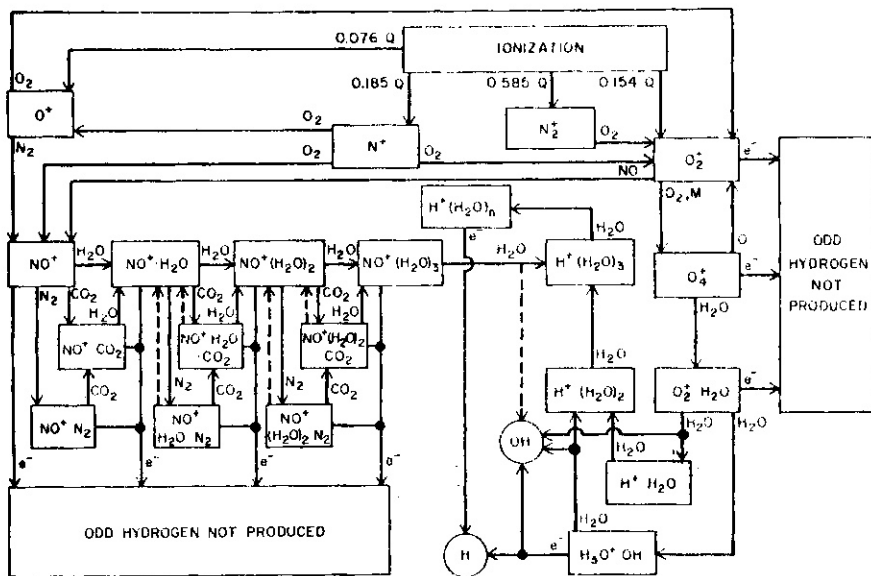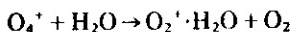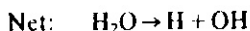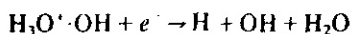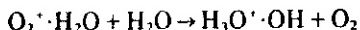§Present address: Max-Planck-Institut für Chemie, Mainz, West Germany.

FIG. 1. SCHEMATIC REPRESENTATION OF THE ION CHEMISTRY LEADING TO ODD HYDROGEN FORMATION.

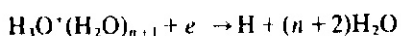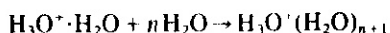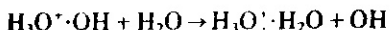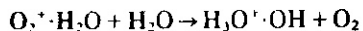formation can be achieved. The remaining portion of the ionization ultimately forms O_2^+ and may potentially form two odd hydrogen particles per unit of charge by a reaction path initiated by:
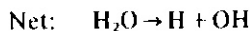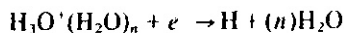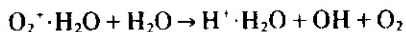
$$O_2^+ + O_2 + M \rightarrow O_4^+ + M$$

$$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$$

and followed by

$$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$$

$$H_3O^+ \cdot OH + e^- \rightarrow H + OH + H_2O$$

Net: $H_2O \rightarrow H + OH$

or by

$$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$$

$$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+ \cdot H_2O + OH$$

$$H_3O^+ \cdot H_2O + nH_2O \rightarrow H_3O^+(H_2O)_{n+1}$$

$$H_3O^+(H_2O)_{n+1} + e^- \rightarrow H + (n+2)H_2O$$

Net: $H_2O \rightarrow H + OH$

or by

$$O_2^+ \cdot H_2O + H_2O \rightarrow H^+ \cdot H_2O + OH + O_2$$

$$H^+ \cdot H_2O + n(H_2O) \rightarrow H_3O^+(H_2O)_n$$

$$H_3O^+(H_2O)_n + e^- \rightarrow H + (n)H_2O$$

Net: $H_2O \rightarrow H + OH$
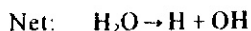
Many of the pathways indicated above involve recombination of positive ions with electrons. It should be noted, however, that below about 70 km, negative ions become more abundant than electrons, so that positive ions will probably recombine with negative ions rather than with electrons. The products and reaction rates of this process currently are not well known, but it is likely that oxonium ions react with the terminal negative ions, NO_3^-, as follows:

$$H^+(H_2O)_n + NO_3^- \rightarrow NHO_3 + nH_2O.$$
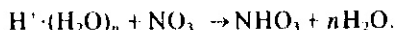
The production of odd hydrogen then depends on the fate of HNO_3. HNO_3 may react with OH as follows:

$$OH + HNO_3 \rightarrow H_2O + NO_3.$$
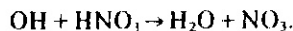
If this occurs, then some odd hydrogen will be destroyed. HNO_3 is, however, more likely to photolyze to yield OH in the upper stratosphere and mesosphere. In this case, as many odd hydrogen particles will be produced per ionization as in the case of recombination of positive ions with electrons. However, there will be some delay in odd

hydrogen production, since the photolysis lifetime of HNO_3 is of the order of hours to days in the region from 65 to 40 km.

To simplify the discussion in this paper, we deal only with recombination of positive ions with electrons. In the calculations, we have not included the kinetics associated with HNO_3 formation by ion reactions, but have instead assumed that recombination of oxonium ions with either electrons or negative ions immediately yields odd hydrogen.

If we neglect for the moment the formation of NO^+ from charge exchange of O_2^+ with NO, the fraction of charge which forms NO^+ is approximately given by:

$$\frac{P_{O^+}}{Q} \cdot \frac{k_{12}[N_2]}{k_{11}[O_2] + k_{12}[N_2]} + \frac{P_{N^+}}{Q} \cdot \alpha = 0.096$$

where Q = total ionization rate; P_{O^+} = production

rate of $O^+ = 0.076 \cdot Q$; P_{N^+} = production rate of $N^+ = 0.185 \cdot Q$; α = branching ratio for NO^+ formation from the reaction $N^+ + O_2$; k_i = rate constant for reaction 1 in Table 1.

The fraction of charge which forms O_2^+ is then $1 - 0.096$ or 0.904. We first consider how much odd hydrogen is formed per O_2^+ ion, and then discuss the production from NO^+. The upper limit for odd hydrogen production via O_2^+ is $2 \cdot (0.094) \cdot Q$ or $1.808 \cdot Q$, which is achieved only if all of the O_2^+ forms O_4^+, which then forms $O_2^+ \cdot H_2O$, and which then reacts with H_2O. As shown in Fig. 1, the chain may be interrupted if $O_2^+ \cdot H_2O$, or O_4^+, or O_2^+ recombines with an electron.

The production of odd hydrogen per ionization from O_2^+ may be approximated as follows:

$$\left(\frac{P_{HO_x}}{Q}\right)_{O_2^+} = \frac{2P_{O_2^+} \alpha_1 \alpha_2 \alpha_3}{Q} \tag{1}$$

TABLE 1. ION REACTION DISCUSSED IN THE TEXT. REACTION RATE CONSTANTS ARE GIVEN BY REID (1976, 1977)

1.	$O_2^+ + O_2 + M \rightarrow O_4^+ + M$
2.	$O_2^+ + e^- \rightarrow 2O$
3.	$O_2^+ + NO \rightarrow NO^+ + O_2$
4.	$O_4^+ + O \rightarrow O_2^+ + O_3$
5.	$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$
6.	$O_2^+ \cdot H_2O + H_2O \rightarrow H^+ \cdot H_2O + OH$
7.	$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$
8.	$H_3O^+ \cdot OH + H_2O \rightarrow H^+ \cdot (H_2O)_2 + OH$
9.	$H_3O^+ \cdot OH + e^- \rightarrow H + OH + H_2O$
10.	$H^+(H_2O)_n + e^- \rightarrow H + nH_2O$
11.	$O^+ + O_2 \rightarrow O_2^+ + O$
12.	$O^+ + N_2 \rightarrow NO^+ + N$
13.	$N^+ + O_2 \rightarrow O^+ + NO$
14.	$N^+ + O_2 \rightarrow O_2^+ + N$
15.	$N^+ + O_2 \rightarrow NO^+ + O$
16.	$NO^+ + e^- \rightarrow N + O$
17.	$NO^+ + CO_2 + M \rightleftarrows NO^+ \cdot CO_2 + M$
18.	$NO^+ + N_2 + M \rightleftarrows NO^+ \cdot N_2 + M$
19.	$NO^+ + H_2O + M \rightleftarrows NO^+ \cdot H_2O + M$
20.	$NO^+ \cdot N_2 + CO_2 \rightarrow NO^+ \cdot CO_2 + N_2$
21.	$NO^+ \cdot CO_2 + H_2O \rightarrow NO^+ \cdot H_2O + CO_2$
22.	$NO^+ \cdot N_2 + H_2O \rightarrow NO^+ \cdot H_2O + N_2$
23.	$NO^+ \cdot H_2O + N_2 + M \rightleftarrows NO^+ \cdot H_2O \cdot N_2 + M$
24.	$NO^+ \cdot H_2O + CO_2 + M \rightleftarrows NO^+ \cdot H_2O \cdot CO_2 + M$
25.	$NO^+ \cdot H_2O + H_2O + M \rightleftarrows NO^+ \cdot (H_2O)_2 + M$
26.	$NO^+ \cdot H_2O \cdot N_2 + CO_2 \rightarrow NO^+ \cdot H_2O \cdot CO_2 + N_2$
27.	$NO^+ \cdot H_2O \cdot CO_2 + H_2O \rightarrow NO^+ \cdot (H_2O)_2 + CO_2$
28.	$NO^+ \cdot H_2O \cdot N_2 + H_2O \rightarrow NO^+ \cdot (H_2O)_2 + N_2$
29.	$NO^+ \cdot (H_2O)_2 + N_2 + M \rightleftarrows NO^+ \cdot (H_2O)_2 \cdot N_2 + M$
30.	$NO^+ \cdot (H_2O)_2 + CO_2 + M \rightleftarrows NO^+ \cdot (H_2O)_2 \cdot CO_2 + M$
31.	$NO^+ \cdot (H_2O)_2 + H_2O + M \rightleftarrows NO^+ \cdot (H_2O)_3 + M$
32.	$NO^+ \cdot (H_2O)_2 \cdot N_2 + CO_2 \rightarrow NO^+ \cdot (H_2O)_2 \cdot CO_2 + N_2$
33.	$NO^+ \cdot (H_2O)_2 \cdot CO_2 + H_2O \rightarrow NO^+ \cdot (H_2O)_3 + CO_2$
34.	$NO^+ \cdot (H_2O)_2 \cdot N_2 + H_2O \rightarrow NO^+ \cdot (H_2O)_3 + N_2$
35.	$NO^+ \cdot (H_2O)_3 + H_2O \rightarrow H^+ \cdot (H_2O)_3 + HNO_2$
36.	$X^+ + e^- \rightarrow PRODUCTS$
37.	$X^+ + X^- \rightarrow PRODUCTS$

where $P_{O_2^+}$ = total rate of production of O_2^+ = $0.904Q + k_4[O_4^+][O]$; α_1 = fraction of O_2^+ which forms O_4^+ instead of recombining or charge exchanging with NO, for example; α_2 = fraction of O_4^+ which forms $O_2^+ \cdot H_2O$; α_3 = fraction of $O_2^+ \cdot H_2O$ which reacts with H_2O.

Considering only the major loss processes for O_2^+, O_4^+ and $O_2^+ \cdot H_2O$. we have:

$$\alpha_1 = \frac{k_1[O_2][M]}{k_2[e^-] + k_1[O_2][M] + k_3[NO]}, \quad (2)$$

$$\alpha_2 = \frac{k_5[H_2O]}{k_4[O] + k_{36}[e^-] + k_5[H_2O]}, \quad (3)$$

$$\alpha_3 = \frac{(k_6 + k_7)[H_2O]}{(k_6 + k_7)[H_2O] + k_{36}[e^-]}. \quad (4)$$

A value of any α which is less than one, indicates that the positive ion chain leading to odd hydrogen may be broken at that point. Lastly, if we consider:

$$[O_4^+] \cong \frac{k_1[O_2^+][O_2][M]}{k_4[O] + k_{36}[e^-] + k_5[H_2O]}, \quad (5)$$

and

$$[O_2^+] \cong \frac{0.904Q + k_4[O_4^+][O]}{k_2[e^-] + k_1[O_2][M] + k_3[NO]}. \quad (6)$$

Substituting (6) in (5), and using (1), we obtain an expression for odd hydrogen produced per ionization from the O_2^+ channel.

O_2^-, and thus there are more intermediates which may recombine with electrons to cut off the chain. We will examine the processes leading from NO^+ to odd hydrogen formation using the chemistry suggested by Reid (1977) in the Appendix.

The total amount of odd hydrogen formed per ionization is the sum of (7) and (8) (derived in the Appendix). These expressions are extremely useful for numerical studies of particle precipitation. If the densities of the neutral components O_2, M, H_2O, NO, and atomic oxygen are measured or estimated from model calculations, then substitution in (7) and (8) yields the odd hydrogen production per ionization if the electron density is known. It should be noted, however, that as a particle precipitation event proceeds, NO is produced (see Rusch *et al.*, 1980), and ozone and atomic oxygen (Swider *et al.*, 1978) as well as water vapor (Crutzen and Solomon, 1980) may be destroyed. Furthermore, the electron density is strongly dependent on the ionization rate and, at lower altitudes, on the ratio between negative ions and electrons. All of these parameters are likely to be functions of time during an actual event, and we consider these effects in more detail below.

RESULTS

The neutral model used in these calculations is the one-dimensional time-dependent model described by Crutzen *et al.* (1978) and Solomon and Crutzen (1980) to which the ion chemical model of Reid (1977) has been coupled. The neutral chemical reaction rates employed are described in Solomon and Crutzen (1980).

$$\left(\frac{P_{HO_2}}{Q}\right)_{O_2^+} = \frac{2 \cdot \left(0.904Q + k_4[O]\left(\frac{0.904Q\alpha_1}{k_{36}[e^-] + k_5[H_2O] + (1 - \alpha_1)k_4[O]}\right)\right)\alpha_1\alpha_2\alpha_3}{Q}. \quad (7)$$

It is somewhat more difficult to evaluate the formation of odd hydrogen from the NO^+ channel. It should be noted that the reaction path from NO^+ to odd hydrogen is somewhat more speculative than that leading from O_2^+ to odd hydrogen, and the reaction rate constants are not well known. This pathway was suggested by Dunkin *et al.* (1971) and Ferguson (1971), and many of the relevant rate constants were proposed by Reid (1977) but have not yet been measured in the laboratory.

As Fig. 1 shows, the chain of reactions which are believed to be followed if odd hydrogen is to be produced is longer in the case of NO^+ than for

Before turning to the time-dependent chemistry of an actual event, we wish to emphasize the effects of altitude and ionization rate on odd hydrogen production even in an unperturbed atmosphere, as occurs at the beginning of an event.

Figure 2 shows the number of odd hydrogen particles produced per ionization as a function of altitude and ionization rate for daytime, polar summer conditions of temperature, air density, and solar zenith angle. In these calculations we have evaluated odd hydrogen produced per ionization (hereafter referred to as P_{HO_x}/Q) by adding
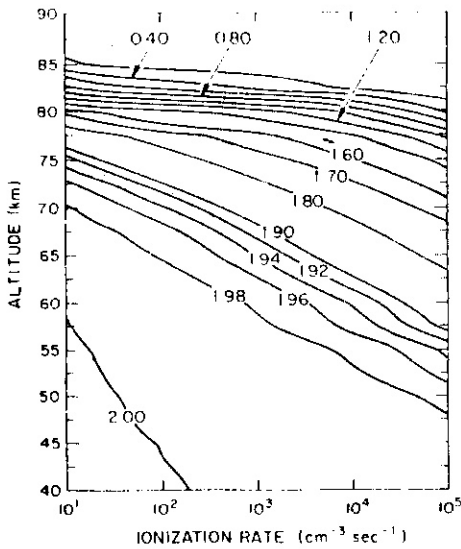
FIG. 2. CONTOURS OF ODD HYDROGEN PARTICLES PRODUCED PER IONIZATION AS A FUNCTION OF ALTITUDE AND IONIZATION RATE FOR DAYTIME SUMMER POLAR CONDITIONS.

up the computed rates of all the ion reactions which produce odd hydrogen (such as $O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot H_2O + OH + O_2$, for example), and we find that this agrees with the approximate expressions, (7) and (8), to within about $0.05 P_{HO_x}/Q$. As the ionization rate increases, the computed electron density increases and the probability of recombination of the O_4^+ and $O_2^+ \cdot H_2O$ intermediates increases. Thus at all altitudes, P_{HO_x}/Q is seen to decrease with increasing ionization rate. The densities of H_2O and O_2 decrease with increasing altitude, while the atomic oxygen and electron density increase, so that for a given ionization rate, P_{HO_x}/Q decreases with altitude. It should be emphasized that the decrease of H_2O with altitude may be strongly dependent on season, latitude, and the rate of vertical transport.

We also wish to note that the reaction of O_4^+ with atomic oxygen does not directly cause decreased odd hydrogen production, since it does not result in the loss of any positive charge from the O_2^+ channel. However, it produces an increased amount of cycling between O_2^+ and O_4^+, thus increasing the time required to complete the reaction chain leading to odd hydrogen, and increasing the probability that recombination will occur before odd hydrogen can be produced. The collisional dissociation of species such as $NO^+ \cdot H_2O \cdot N_2$ yields the same result for the NO^+ chain.

We now illustrate the nature of possible diurnal and time dependent factors by considering a hypothetical event of constant ionization rate in altitude and time of $5 \cdot 10^3$ ion pairs cm^{-3} s^{-1}. The altitude profile of temperature and air density represent March, 70°N latitude; conditions as given by CIRA (1972).

The calculated behavior of P_{HO_x}/Q is shown in Fig. 3 for a number of altitudes. The first 6 h here are night, followed by 12 h of day, 12 h of night, etc. The decline in P_{HO_x}/Q with increasing altitude is clearly seen as in Fig. 2. A pronounced diurnal variation occurs above about 70 km, and is due primarily to two factors.

As Bailey (1959) first indicated, the concentration of free electrons undergoes a large decrease at night. Reid (1976) has discussed the ion chemistry responsible for this feature, which is believed to be due to increases in the negative ion-electron ratio. Many of the chemical detachment processes for negative ions involve reactions with atomic oxygen. At night in the D-region, atomic oxygen is converted to ozone, and photodetachment and collisional detachment of negative ions stops, resulting in increased negative ion and decreased electron concentrations. As equations (7) and (8) show, decreased electron concentrations should increase P_{HO_x}/Q (see also the expressions for α_1, α_2, α_3, β_1, β_2, and β_3) by lowering the probability of recombination of intermediates such as $O_2^+ \cdot H_2O$, for example.

The diurnal variation in atomic oxygen discussed above also becomes important in another way. Above about 75 km altitude, daytime atomic oxygen concentrations are large enough to affect odd hydrogen production through reaction with
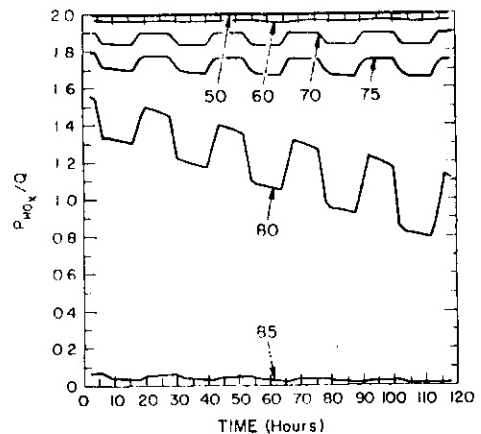

FIG. 3. ODD HYDROGEN PARTICLES PRODUCED PER IONIZATION AS A FUNCTION OF TIME FOR A TEST CASE WITH A CONSTANT IONIZATION RATE OF 5×10^3, SPRING POLAR CONDITIONS.
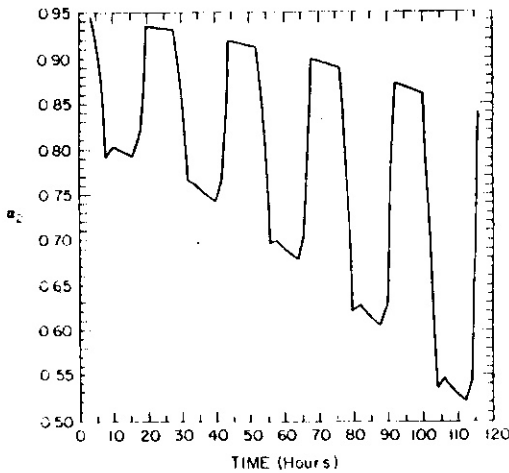
FIG. 4. BEHAVIOR OF α_2 VS TIME AT 80 km FOR THE EVENT
SHOWN IN FIG. 3.

O_4^+ as discussed above (Fehsenfeld and Ferguson, 1972). Thus the diurnal variation seen at high altitudes reflects mostly the impact of this process. Figure 4 shows the calculated time variation in α_2 at 80 km, which illustrates the effect more clearly.

A general downward trend in P_{HO_x}/Q can also be seen above 75 km in Fig. 3 as the event proceeds. As Crutzen and Solomon (1980) indicate, decreased water vapor concentrations may be expected in this region following large amounts of ionization due to the HO, chemistry. This affects the water clustering processes which must occur if odd hydrogen is to be produced. Figure 5 shows the calculated changes in atomic oxygen, nitric oxide, and water vapor at 80 km during this simulation. The diurnal variation in atomic oxygen is clearly seen as well as the gradual depletion of
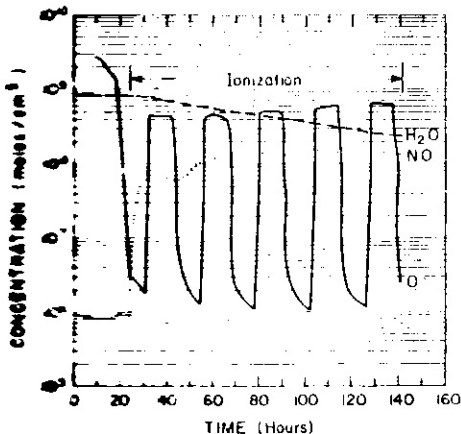

FIG. 5. CALCULATED TIME BEHAVIOR OF O, H_2O, AND NO AT 80 km FOR THE EVENT SHOWN IN FIG. 3.

water vapor. Nitric oxide increases but rapidly saturates at this altitude as explained in paper 1 of this series (Rusch *et al.*, 1980). If larger concentrations of NO occurred at these altitudes, then it could affect odd hydrogen formation at high altitudes by charge exchange of O_2^+ with NO (reaction 3) which diverts some charge from the O_2^+ to the NO^+ channel. We emphasize that the saturation process which results in relatively small NO densities should prevent this from becoming important for most PCA's.

These possible variations in P_{HO_x}/Q with altitude and time will certainly not profoundly affect calculated ozone depletions resulting from PCA activity, particularly below about 75 km. Calculated odd hydrogen concentrations and their diurnal variations during an intense PCA around 80 km altitude will be somewhat different from those obtained assuming two odd hydrogen particles are always produced per ionization, however. Thus observations of such factors as the Meinel band emission from vibrationally excited OH may be affected.

RESULTS FOR THE SOLAR PROTON EVENT OF NOVEMBER 1969

During the solar proton event of November, 1969, decreased ozone concentrations were observed in the 50–70 km region at Fort Churchill, Canada (Weeks *et al.*, 1972). Swider and Keneshea (1973) suggested that this effect was due to enhancement of the HO, catalyzed destruction of odd oxygen $(O + O_3)$ in this region, through catalytic odd oxygen destroying processes such as:

$$OH + O \rightarrow H + O_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + O \rightarrow OH + O_2$$

$$\text{Net:} \qquad 2O \rightarrow O_2$$
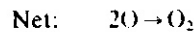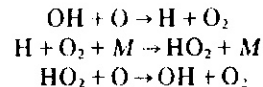
The production of odd hydrogen by the ionization should enhance the concentrations of OH and HO_2, thus increasing the effectiveness of the catalytic cycle and decreasing odd oxygen.

In their analysis of this event, Swider *et al.* (1978) assumed that two odd hydrogen particles were produced per ionization, and they predicted a decrease in ozone at 70 km during the PCA of about a factor of two as opposed to a factor of four in the data. Figure 6 shows our computed number of odd hydrogen particles per ionization at 70 km as a function of time during this event. P_{HO_x}/Q ranges from about 1.8 to 1.9. The ion-
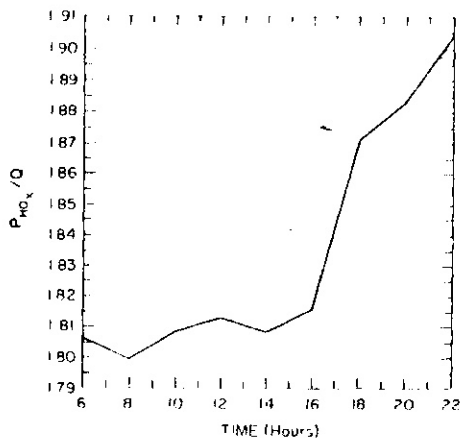
Fig. 6. Odd hydrogen particles produced per ion-
ization at 70 km as a function of time for the 3
November 1969 solar proton event. Sunset
occurs around 1600 CST.

ization rates used here were based on data from
the IMP satellite experiment (Solar Geophysical
Data, 1970) and were supplied to us by Charles
Jackman (private communication). Temperature
and air density were taken from CIRA (1972) for
60°N, November conditions. Sunset occurs at
about 1600 cst, and an increase in P_{HO_x}/Q can
be seen after dark as discussed above.

Figure 7 shows the calculated time behavior of
HO_x, O_3, and NO_x at 70 km during the event, and
the ozone observed by Weeks et al. (1972) is also
indicated. Our results are not much different from
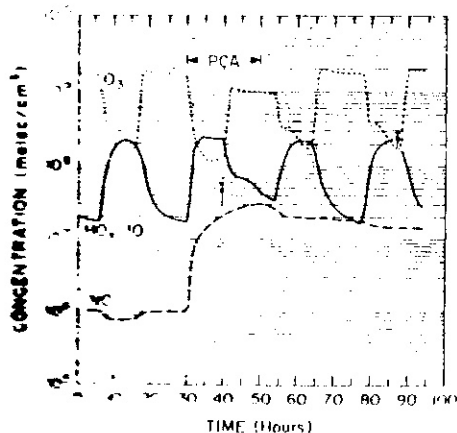the previous analysis by Swider et al. (1978) even

Fig. 7. Calculated time behavior of O_3, HO_x, and NO_x
at 70 km for the November 1969 PCA for several days
before, during and after the event. The observations
of Weeks et al. (1972) are indicated by the filled cir-
cles with error bars.

though we calculate 1.8 odd hydrogen particles per
ionization rather than two. As the behavior of HO_x
in Fig. 7 shows, the concentration of HO_x does not
increase greatly as a result of the ionization. This
is because the natural background production rate
of odd hydrogen from the photolysis of water
vapor and reaction of water vapor with $O(^1D)$ is
greater than the ionization source in this particular
event. The comparison between experiment and
theory in this case is therefore probably strongly
dependent on the adopted chemistry of odd
hydrogen partitioning, production and loss pro-
cesses (e.g. such factors as the background con-
centrations of H_2O and O_3, and the rate coefficient
for the reaction of OH with HO_2 may play an
important role).

As an example, we have explored the sensitivity
of the calculated results to the water vapor mixing
ratio. The rate of production of odd hydrogen
through ion reactions occurring during the SPE
should be compared to the rate of production from
the oxidation and photolysis of water vapor,

$$O(^1D) + H_2O \longrightarrow 2OH$$
$$H_2O + h\nu \longrightarrow H + OH.$$
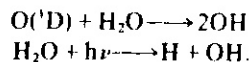
At 70 km during this event, the maximum rate of
odd hydrogen production from ionization is about
1300 molecules cm^{-3}s^{-1}, while the rate of odd
hydrogen production from water vapor destruction
is about 10,000 molecules cm^{-3}s^{-1}. Thus the pro-
duction rate of odd hydrogen induced by the SPE
is only about 10% of the daytime natural background
production rate, and therefore odd hydrogen con-
centrations are not dramatically affected by the
SPE, as can be seen in Fig. 7. The calculated water
vapor mixing ratio at 70 km in this calculation is
about 4 ppm. Only if the water vapor mixing ratios
were an order of magnitude lower than calculated
in the model, could the odd hydrogen production
rate by the SPE be comparable to the natural
background production rate from water vapor.
This is not consistent with current measurements
(e.g. Arnold and Krankowsky, 1977). Such an ex-
treme change in water vapor mixing ratios would
result in large changes of odd hydrogen densities
during the SPE. The relative change in ozone
density during the disturbance compared to the quiet
day would then be similar to the measurements, but
the absolute density for the undisturbed day would
be larger (about a factor of 3) than the measured
value shown in Fig. 7.

Faire and Murphy (1972) measured temperatures
on several rocket flights at Fort Churchill during

this SPE. They observed increases in temperature of about 15 K below 70 km on the most disturbed day. Such a change in temperature may be expected to result in a change in local air density. This affects the partitioning of odd oxygen through the reaction $O + O_2 + M \rightarrow O_3 + M$, which maintains the ratio between atomic oxygen and ozone. Since the atomic oxygen concentration is expected to be larger than the ozone concentration at 70 km, changes in the ratio between them may affect the ozone significantly even if the total odd oxygen density is constant. Furthermore, such temperature changes may be associated with changes in the vertical wind speed, and so transport processes may influence the ozone density.

DISCUSSION

We have examined the ion and neutral chemistry associated with odd hydrogen production during charged particle precipitation. We have shown that the odd hydrogen produced per ion pair may vary in time and altitude during a particle precipitation event as a result of change in the ionization rate, water vapor density, and atomic oxygen density, particularly at altitudes above about 75 km. Thus, we have examined the validity of assuming a production of odd hydrogen normalized to the ionization rate, as we did for odd nitrogen in paper I of this series. We conclude that, in general below about 60 km, and for reasonable values of the ionization rate, nearly two odd hydrogen particles are indeed produced per ionization, while somewhat less than two may be obtained at higher altitudes. Diurnal effects relating to the negative ion–electron ratio at altitudes between about 65 and 75 km, and the atomic oxygen density above about 80 km may also influence odd hydrogen production somewhat.

The consideration of these effects does not significantly influence the comparison of calculated and observed ozone depletion at 70 km for the November 1969 PCA. It should become important for ozone depletion calculations at higher altitudes or for events exhibiting higher ionization rates, and should also influence calculated odd hydrogen densities during such an event.

useful discussions. We also thank F. Fehsenfeld for pointing out the importance of negative ion recombination with oxonium ions.

REFERENCES

Arnold, F. and Krankowsky, D. (1977). Ion composition and electron and ion loss processes in the Earth's atmosphere, in *Dynamical and Chemical Coupling Between the Neutral and Ionized Atmosphere* (Ed. B. Grandal and A. Holtet) p. 93. Reidel, New York.

Bailey, D. K. (1959). *Proc. Inst. Radio Engrs.* **47**, 255.

CIRA (1972). *COSPAR International Reference Atmosphere*, Akademie, Berlin.

Crutzen, P. J., Isaksen, I. S. A. and McAfee, J. R. (1978). *J. geophys. Res.* **83**, 345.

Crutzen, P. J. and Solomon, S. (1980). *Planet. Space Sci.*, **28**, 1147.

Dunkin, D. B., Fehsenfeld, F. C., Schmeltekopf, A. L. and Ferguson, E. E. (1971). *J. Chem. Phys.* **54**, 3817.

Faire, A. C. and Murphy, E. A. (1972). In *Proc. COSPAR Symp. on Solar Proton Event of Nov. 1969* (Ed. J. C. Ulwick), p. 445. AFCRL-72-0494.

Fehsenfeld, F. C. and Ferguson, E. E. (1972) *Radio Sci.* **7**, 113.

Ferguson, E. E. (1971). *Rev. Geophys. Space Phys.* **9**, 997.

Frederick, J. E. (1976). *J. geophys. Res.* **81**, 3179.

Reid, G. C. (1972). In *Magnetosphere-Ionosphere Interactions* (Ed. K. Folkestad), pp. 39–46, Universitetsforlaget, Oslo.

Reid, G. C. (1976). *Adv. At. Mol. Phys.* **12**, 375.

Reid, G. C. (1977). *Planet. Space Sci.* **25**, 275.

Rusch, D. W., Gérard, J. C., Solomon, S., Crutzen, P. J. and Reid, G. C. (1980). submitted, *Planet. Space Sci.*

Solar Geophysical Data (1970). 039, Pt. 2, pp 78–83, U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Environmental Data Service.

Solomon, S. and Crutzen, P. J. (1981). *J. geophys. Res.* **86**, 1140.

Swider, W. and Keneshea, T. J. (1973). *Planet. Space Sci.* **21**, 1969.

Swider, W., Keneshea, T. J. and Foley, C. I. (1978). *Planet. Space Sci.* **26**, 883.

Weeks, L. H., Cuikay, R. S. and Corbin, J. R. L. (1972). *J. Atmos. Sci.* **29**, 1138.

APPENDIX

In order to produce odd hydrogen, the third hydrate of NO^+, $NO^+ \cdot (H_2O)_3$ must be formed. This implies that the NO^+ formed must go through three successive reaction sequences of the form:

$$NO^+(H_2O)_n + X \rightleftharpoons NO^+(H_2O)_n \cdot X \xrightarrow[H_2O]{M} NO^+(H_2O)_{n+1}$$
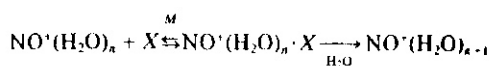
$$X = CO_2, N_2$$

where $n = 0, 1,$ or 2.

In general, the switching reactions such as $NO^+ \cdot H_2O \cdot N_2 + CO_2$ are sufficiently fast that the only competitive process is the collisional detachment of $NO^+(H_2O)_n \cdot X$. Furthermore, the first of the three sequences $(n = 0)$ is so fast below about 90 km that

nearly all of the NO$^+$ formed becomes NO$^+ \cdot H_2O$ even during an intense SPE, where electron densities are large. We must then examine how much NO$^+ \cdot H_2O$ will become NO$^+(H_2O)_2$ as opposed to the fraction which will be lost through recombination.

The following loss and production processes can be formulated from the reactions list in Table 1:

$$L_{NO^+ \cdot H_2O} = \{k_{23}[N_2] + k_{24}[CO_2] + k_{25}[H_2O]\}[M] + k_{36}[e^-]$$

$$L_{NO^+ \cdot H_2O \cdot CO_2} = \{k_{26}[M] + k_{27}[H_2O] + k_{36}[e^-]\}$$

$$L_{NO^+ \cdot H_2O \cdot N_2} = \{k_{25}[M] + k_{28}[H_2O] + k_{36}[e^-]\}$$

$$P_{NO^+ \cdot H_2O \cdot N_2} = \{k_{13}[NO^+ \cdot H_2O][N_2][M]\} = \gamma_1 \cdot [NO^+ \cdot H_2O]$$

$$P_{NO^+ \cdot H_2O \cdot CO_2} = k_{24}[NO^+ \cdot H_2O] \cdot [CO_2] \cdot [M] + k_{26}[NO^+ \cdot H_2O \cdot N_2][CO_2]$$

then, the fraction of NO$^+ \cdot H_2O$ which finally forms NO$^+(H_2O)_2$ rather than recombining is given by:

$$\beta_1 = 1 - \cfrac{k_{36}[e^-]}{L_{NO^+ \cdot H_2O} - [M]\left(\cfrac{k_{23}\gamma_1}{L_{NO^+ \cdot H_2O \cdot N_2}} + \cfrac{k_{24}(k_{24}[CO_2][M] + k_{26}[CO_2]) - \cfrac{\gamma_1}{L_{NO^+ \cdot H_2O \cdot N_2}}}{L_{NO^+ \cdot H_2O \cdot CO_2}}\right)}$$

For the third sequence describing NO$^+(H_2O)_2 \to NO^+(H_2O)_3$, a similar expression can be shown to be:

$$\beta_2 = 1 - \cfrac{k_{36}[e^-]}{L_{NO^+ (H_2O)_2} - [M]\left(\cfrac{k_{29}\gamma_2}{L_{NO^+ (H_2O)_2 \cdot N_2}} + \cfrac{k_{30}(k_{30}[CO_2][M] + k_{32}(CO_2)) - \cfrac{\gamma_2}{L_{NO^+ (H_2O)_2 \cdot N_2}}}{L_{NO^+ (H_2O)_2 \cdot CO_2}}\right)}$$

Finally, the NO$^+(H_2O)_3$ may recombine rather than reacting with H$_2$O to produce H$^+(H_2O)_3$ and HNO$_2$, (which very **rapidly** photolyzes to form odd hydrogen). This leads to a third fraction, β_3:

$$\beta_3 = \frac{k_{35}[H_2O]}{k_{35}[H_2O] + k_{36}[e^-]}.$$

Thus, the odd hydrogen production from the NO$^+$ channel is:

$$\left(\frac{P_{HO_x}}{Q}\right)_{NO^+} = 2 \cdot \frac{P_{NO^+}}{Q}\beta_1\beta_2\beta_3$$

$$P_{NO^+} = 0.096Q + k_3[O_2^+][NO].$$

Substituting for O$_2^+$ from the expressions above, we have:

$$\left(\frac{P_{HO_x}}{Q}\right)_{NO^+} = 2 \cdot (0.096 + k_1[NO]) \cdot \frac{0.904Q + k_4[O] \cdot \cfrac{a_1 \cdot 0.904Q}{k_{36}[e^-] + k_5[H_2O] + (1 - a_1)k_4[O]}}{k_2[e^-] + k_1[O_2][M] + k_1[NO]}\beta_1\beta_2\beta_3 \tag{8}$$