

THE EFFECT OF PARTICLE PRECIPITATION EVENTS ON THE NEUTRAL AND ION CHEMISTRY OF THE MIDDLE ATMOSPHERE—I. ODD NITROGEN

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Abstract—A one-dimensional, time-dependent model of the neutral and ion composition of the middle atmosphere is used to study the processes controlling the production and loss of odd nitrogen species during particle ionization events. From consideration of the cross-sections for the relevant ionization and dissociation reactions we conclude that between 1.3 and 1.6 odd nitrogen atoms per ion pair are produced in the middle atmosphere. The value in the thermosphere is larger due to the role of atomic oxygen. The time-dependent mutual destruction of odd nitrogen by the reaction $N(^4S) + NO \rightarrow N_2 + O$ must be included and the assumption of a nitric oxide production normalized to the ionization rate is invalid. A simulation of the 1972 August solar proton event is presented. The calculated ozone depletion occurring during the event due to the increase in odd nitrogen agrees well with the measured ozone changes.

INTRODUCTION

The production of minor species (odd hydrogen and odd nitrogen) in the Earth's atmosphere subject to particle bombardment has been intensely studied in recent years. These studies have been motivated by measurements of anomalously large densities of odd nitrogen species under auroral conditions, and the observed decreases in ozone resulting from atmospheric ionization. The entire system is complex, involving the degradation of primary particles, the effect of secondary electrons on atmospheric species, ionospheric chemistry including complicated cluster ion chemistry, the production of odd hydrogen, nitrogen, and oxygen species, their chemical interactions and their eventual chemical loss and transport.

In the thermosphere, odd nitrogen [$N(^2D)$, $N(^4S)$, NO] production subsequent to ionization by auroral electrons has been investigated theoretically by Hyman *et al.* (1976), Roble and Rees (1977), Gérard and Barth (1977), Gérard and Rusch (1979), Rusch and Gérard (1980), and Roble and Gary (1979). They have attempted to explain observations of anomalously high $[NO^+]/[O_2^+]$ ratios

by Donahue *et al.* (1970), Narcisi and Swider (1976), Swider and Narcisi (1977), and Sharp *et al.* (1979) and measurements of NO densities, Rusch and Barth (1975) and Sharp (1978).

In the mesosphere and stratosphere interest in odd nitrogen [NO , $N(^4S)$, $N(^2D)$, NO_2 , NO_3 , N_2O_3] and odd hydrogen [H , OH , HO_2 , H_2O_2] production by particle events was stimulated by the observations of Weeks *et al.* (1972) of ozone depletions during a proton event and the recognition of the catalytic nature of the reaction of odd nitrogen species and ozone (Crutzen, 1970). Attempts to assess quantitatively the production of odd nitrogen and the subsequent depletion of ozone were made by Crutzen *et al.* (1975), Reid *et al.* (1976), Frederick (1976), Heath *et al.* (1977), Reagen *et al.* (1978), Fabian *et al.* (1979), Bauer (1979), and Solomon and Crutzen (1981). Thorne (1980) has reviewed several aspects of particle precipitation and its effects on the chemical composition of the middle atmosphere.

Calculations of odd nitrogen production in the thermosphere have taken into account the full complexity of ionospheric chemistry resulting from the particle precipitation event (see e.g. Roble and Rees, 1977; Gérard and Rusch, 1979). Similar calculations in stratospheric models employ neutral odd nitrogen and partial ion chemistry (Crutzen *et al.*, 1975; Frederick, 1976; Reagen *et al.*, 1978), or assume a production of NO normalized to the ionization rate. Bauer (1979) recommended 1.3 NO molecules per ionization, Fabian *et al.* (1979) assumed 2–2.5 NO molecules per ionization, and Solomon and Crutzen (1981) assumed 1.5 NO

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molecules/ionization. In addition, a recent theoretical study by Porter *et al.* (1976) gives a value of 1.27 odd nitrogen atoms per ion pair in proton ionization events.

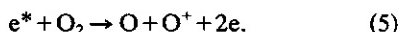
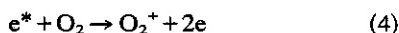
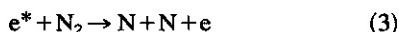
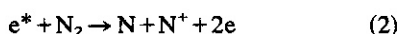
In this paper, we calculate the time-dependent concentrations of odd nitrogen as a result of ionization processes in the middle atmosphere including the relevant ion chemistry and compare the results with previous assumptions to evaluate the validity of assuming a constant production of N atoms per ion pair created as a function of altitude, time, and ionization intensity. A new calculation of the ozone depletion during the August 1972 solar proton event is also presented.

In future papers, we will present detailed studies of the nature of odd hydrogen and complex ion chemistry produced by particle ionization.

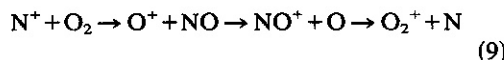
THE MODEL

The model used in these calculations is the one-dimensional, time-dependent model described in Crutzen *et al.* (1978) and Solomon and Crutzen (1981) extended to include the nitrogen-oxygen ion chemistry. The densities of N_2^+ , NO^+ , O_2^+ , N^+ , O^+ , $N(^4S)$, $N(^2D)$ and NO are calculated from the time-dependent ionization rates and the chemistry described below. The model includes current odd nitrogen, odd hydrogen, odd oxygen and odd chlorine chemistry. Background atmospheric composition before the event is that of Model D in Solomon and Crutzen (1981).

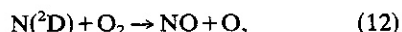
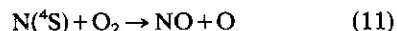
The ion and neutral odd-nitrogen chemistry is initiated in particle events by the action of energetic secondary electrons, e^* , on the major atmospheric species:



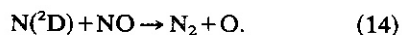
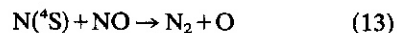
This is followed by a series of interchange and recombination reactions involving nitrogen and its ions which produce additional atomic nitrogen:



where the resulting atomic nitrogen atoms may be formed either in the ground 4S level or excited to the 2D level. Nitric oxide is subsequently formed by the reaction of atomic nitrogen with O_2 :



where reaction (12) is much faster than reaction (11) at stratospheric and mesospheric temperatures. The mutual destruction of odd nitrogen occurs through the following reactions:



The rate constants and temperature dependences of reactions (6)–(14) have been measured in the laboratory or deduced by analysis of Atmosphere Explorer measurements of thermospheric ion chemistry. However, the branching ratios for $N(^2D)$ production of reactions (2), (3), (6), (7), and (9) have not been experimentally determined. Only in the case of dissociative recombination of NO^+ [reaction (10)] is there any laboratory guidance. Kley *et al.* (1977) have found that 75% of the nitrogen atoms are formed in the 2D level. Choices of efficiencies for the rest must be guided by indirect evidence of the daytime and auroral odd nitrogen chemistry (see e.g. Gérard and Rusch, 1979; Rusch and Gérard, 1980). We have adopted branching ratios for $N(^2D)$ production of 100% for reaction (6) and 50% for reaction (7).

We present calculations for two different branching ratios for the combined effect of reactions (2) and (3). Reaction (8) is energetically incapable of $N(^2D)$ production. The third channel of reaction (9) is assumed to be 100% efficient in $N(^4S)$ production but provides only a minor contribution to the total odd nitrogen production.

An important quantity in this study is the number of nitrogen atoms produced for each ion pair created by the primary and secondary particles. The N_2 and O_2 total ionization rates are assumed to be proportional to the mass of the target particle and are given by:

$$Q(N_2) = Q \frac{0.88[N_2]}{0.88[N_2] + [O_2]}$$

$$Q(O_2) = Q \frac{[O_2]}{0.88[N_2] + [O_2]}$$

where Q is the total ionization rate (Vallance Jones, 1975).

The relative magnitude of the ionization and dissociative ionization cross-section [processes (1), (2), (4) and (5)] are in the ratio 0.76:0.24 for N_2 and 0.67:0.33 for O_2 according to Rapp *et al.* (1965).

Taking the ion production rates as proportional to the cross-section, one obtains in the homosphere:

$$P(N_2^+) = 0.76 \times 0.77Q = 0.585Q$$

$$P(N^+) = 0.24 \times 0.77Q = 0.185Q$$

$$P(O_2^+) = 0.67 \times 0.23Q = 0.154Q$$

$$P(O^+) = 0.33 \times 0.23Q = 0.076Q.$$

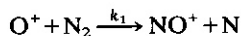
The sources of nitrogen atoms are dissociation and dissociative ionization of N_2 (reactions (2) and (3)) and reactions (8) and (9). The number of N atoms produced by dissociation of N_2 is approximately given by:

$$P_1(N) = 2D(N_2) = \frac{2\sigma_D}{\sigma_I} Q(N_2),$$

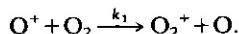
where $D(N_2)$ is the dissociation rate of N_2 , and σ_D and σ_I are the peak values of the dissociation and total ionization cross-sections, respectively. Various determinations of σ_D have been made. Winters (1966) has measured the total dissociation cross-section [including the branch described by reaction (2)] and obtained a peak value of $2.0 \times 10^{-16} \text{ cm}^2$ at about 90 eV. A similar result was obtained by Niehaus (1967). Subtracting the value of the dissociative ionization cross-section (Rapp *et al.*, 1965), a value of $1.4 \times 10^{-16} \text{ cm}^2$ is obtained for the dissociation cross-section. More recently, Zipf and McLaughlin (1978) studied the dissociation of N_2 by electron impact and e.u.v. photo-absorption. From these measurements and the analysis by Zipf *et al.* (1980), the values of $2.27 \times 10^{-16} \text{ cm}^2$ and $2.0 \times 10^{-16} \text{ cm}^2$ are obtained for the total and for the dissociation cross-sections of N_2 , respectively. Measurements of σ_I have been reviewed by Kieffer and Dunn (1966) and we adopt the value of $2.55 \times 10^{-16} \text{ cm}^2$. Consequently, $P_1(N)$ may be estimated to vary between $0.8Q$ and $1.21Q$.

N_2^+ ions readily charge transfer with O_2 to form O_2^+ and make no contribution to the N budget except for a negligibly small fraction due to N_2^+ dissociative recombination [reaction (7)].

Atomic oxygen ions react with the major constituents to give:



or



Thus, the production of N atoms from this second source is:

$$P_2(N) = 2 \frac{k_1[N_2]}{k_1[N_2] + k_2[O_2]} P(O^+) = 0.03Q.$$

Finally, loss of N^+ ions proceeds through three different channels [reactions (9)], all of which ultimately produce an odd nitrogen. Consequently, the production of odd nitrogen resulting from dissociative ionization is:

$$P_3(N) = 2P(N^+) = 0.37Q$$

The total N atom production per ion pair is thus:

$$\frac{P(N)}{Q} = \frac{P_1 + P_2 + P_3}{Q},$$

whose value ranges between 1.31 and 1.61, depending on the value adopted for the dissociation cross-section of N_2 . In the following discussion we adopt the lower value of 1.31 for the number of N atoms produced per ion pair. This value is close to the 1.27 N atoms/ion pair calculated by Porter *et al.* (1976) from energy degradation calculations.

RESULTS

We illustrate the results by first considering an event of constant ionization rate in altitude and time of 5×10^3 ion pairs $\text{cm}^{-3} \text{ s}^{-1}$ for conditions appropriate for the August 1972 proton event to be discussed later. The time rate of change of odd nitrogen can be written

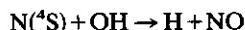
$$\frac{d[NO_x]}{dt} = P_{NO_x} - 2k[N(^4S)][NO], \quad (15)$$

where P_{NO_x} is the production of odd nitrogen per ion pair and k is the rate coefficient for reaction (13).

The ground-state atomic nitrogen density is to a good approximation in photochemical equilibrium and is equal to

$$[N(^4S)] = \frac{J_{NO}[NO] + P_{N^4S}}{k[NO] + k'[O_2]} \quad (16)$$

where P_{N^4S} is the production rate of $N(^4S)$ due to particle precipitation, k' is the rate coefficient for reaction (11), and J_{NO} is the photodissociation frequency of NO. Here we neglect the reaction





which can affect the loss process of $N(^4S)$ although it is included in the model. Upon substitution of equation (16) into equation (15), we can solve for the equilibrium or saturation concentration of NO under sunlight conditions:

$$\frac{d[\text{NO}_x]}{dt} = P_{\text{NO}_x} - 2k \left\{ \frac{P_{N^4S} + J_{\text{NO}}[\text{NO}]}{k[\text{NO}] + k'[\text{O}_2]} \right\} [\text{NO}]. \quad (17)$$

Saturation is achieved when the time derivative is zero. If F is the fraction of odd nitrogen produced in the 4S state, then for saturation

$$2J_{\text{NO}}k[\text{NO}]^2 + (2F-1)kP_{\text{NO}_x}[\text{NO}] - k'P_{\text{NO}_x}[\text{O}_2] = 0. \quad (18)$$

For $F=0.5$, equation (18) becomes

$$[\text{NO}]_{\text{eq}} = \left[\frac{k'[\text{O}_2]P_{\text{NO}_x}}{2J_{\text{NO}}k} \right]^{1/2}. \quad (19)$$

In addition, the characteristic time required to achieve saturation for constant ionization can be written as

$$\tau = [\text{NO}_x]_{\text{eq}} / P_{\text{NO}_x}. \quad (20)$$

In Table 1, we present the calculated equilibrium concentrations of NO and NO_x and the characteristic saturation time for $F=0.5$, an ionization of 5×10^3 ions $\text{cm}^{-3} \text{s}^{-1}$ and a production of NO_x equal to 1.3 times the ionization rate. Saturation for NO occurs rapidly at high altitudes and exceeds the length of the calculation at low altitudes.

We define the efficiency with which odd nitrogen is produced at time t after time increment Δt as

$$E = \frac{[\text{NO}_x(t)] - [\text{NO}_x(t - \Delta t)]}{P_{\text{NO}_x} \Delta t}. \quad (21)$$

An efficiency of one implies that all the odd nitrogen created in the interval Δt is present at the end of the interval. An efficiency less than one implies that a fraction of the odd nitrogen produced during Δt is destroyed by chemical reactions while an efficiency of zero implies the atmosphere is

TABLE 1. EQUILIBRIUM DENSITIES FOR NO AND NO_x AND SATURATION TIME CONSTANTS

Altitude (km)	$[\text{NO}]_{\text{eq}}$ (cm^{-3})	$[\text{NO}_x]_{\text{eq}}$ (cm^{-3})	τ (s)
80	9.4(6)*	1.9(7)	3.1(3)
70	1.7(8)	1.7(8)	2.8(4)
60	1.8(9)	1.8(9)	3.0(5)
50	8.0(9)	8.0(9)	1.3(6)
40	1.2(10)	1.6(10)	2.6(6)

* Read 9.4(6) as 9.4×10^6 .

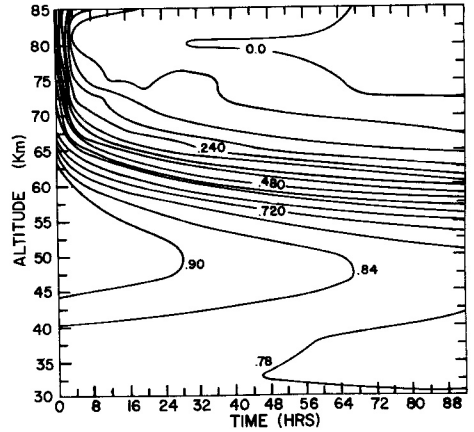


FIG. 1. CONTOURS OF EFFICIENCY OF ODD NITROGEN PRODUCTION IN ALTITUDE AND TIME FOR A CONSTANT IONIZATION RATE.

saturated in odd nitrogen. For the constant ionization calculation, contours of efficiency in time and altitude are presented in Fig. 1, and the time dependence of E at several altitudes is shown in Fig. 2. The figures reveal that saturation is not reached below about 55 km for the entire length of the calculation. Above 60 km, saturation is reached rapidly. The saturation time constant is, of course, ionization rate dependent.

The efficiency for odd nitrogen production can be estimated during a given time increment without the use of a numerical model. Rewriting equation (17) for $P_{N^4S} \gg J_{\text{NO}}$ we have

$$\frac{d[\text{NO}_x]}{dt} = P_{\text{NO}_x} - \frac{2k[\text{NO}]P_{N^4S}}{k'[\text{O}_2] + k[\text{NO}]}. \quad (22)$$

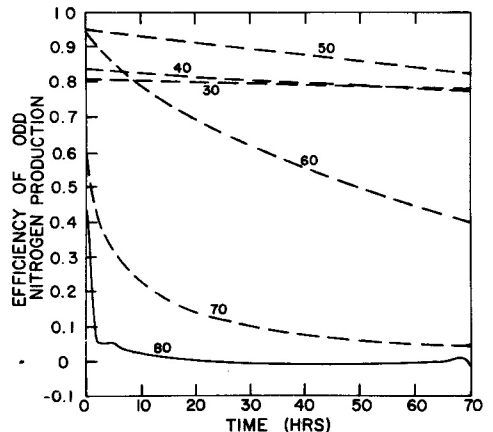


FIG. 2. THE EFFICIENCY OF ODD NITROGEN PRODUCTION VS TIME INTO THE EVENT FOR SIX ALTITUDES.

The curves are marked with the altitude.

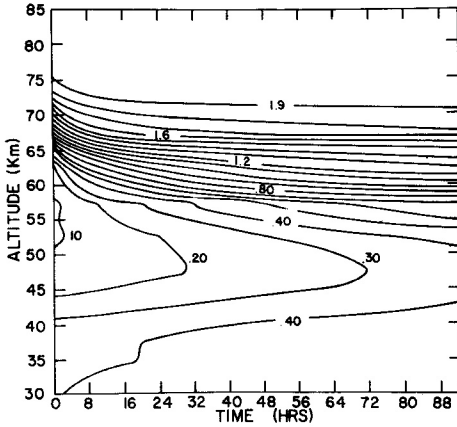


FIG. 3. CONTOURS OF $2k[\text{NO}]/(k'[\text{O}_2] + k[\text{NO}])$ FOR $F = 0.5$ AND A CONSTANT IONIZATION RATE.

Dividing by P_{NO_x} we have

$$E \equiv \frac{d[\text{NO}_x]/dt}{P_{\text{NO}_x}} = 1 - \left\{ \frac{2k[\text{NO}]}{k'[\text{O}_2] + k[\text{NO}]} \right\} \cdot F, \quad (23)$$

where F is the fraction of odd nitrogen produced as $\text{N}(^4\text{S})$. In Fig. 3 we display contours of the term in brackets on the right side of equation (23). For a value of F equal to 0.5, it can be seen that the efficiencies estimated by this simple relationship are quite close to those shown in Fig. 1.

The August 1972 solar proton event has been modeled using the time- and altitude-dependent ionization rates supplied by R. C. Gunton (private communication) which are close to those of Reagen *et al.* (1978). In Fig. 4 we present contours of the ionization rate for the first 4 days of the event. The ionization maximizes during the last half of August 4 but is highly structured throughout the event.

In Fig. 5 we show contours of efficiency for the 1972 event as defined by equation (21) for $\Delta t = 2$ h. The most striking feature is the occurrence of negative efficiencies above 55 km after 4 August and at 35 km early on August 7. Changes in the efficiency with time at a given altitude are correlated to changes in the ionization rate and the current nitric oxide density compared with its saturation value. The loss of odd nitrogen is dependent on the concentration of $\text{N}(^4\text{S})$. Thus when the rate of production of $\text{N}(^4\text{S})$ from photolysis of NO becomes larger than the rate of production of NO due to ionization, more odd nitrogen can be destroyed chemically than is produced in Δt and negative efficiencies result.

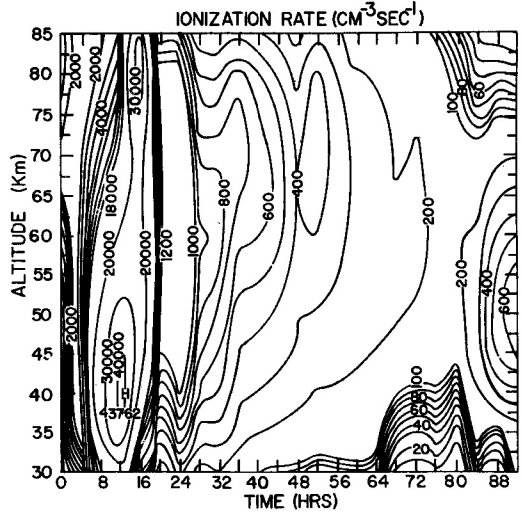


FIG. 4. CONTOURS OF IONIZATION RATE IN UNITS OF IONIZATIONS $\text{cm}^{-3}\text{s}^{-1}$ FOR THE FIRST 4 DAYS OF THE AUGUST 1972 PROTON EVENT.

Time 0 is 4 August 1972 at 339 U.T.

The total amount of odd nitrogen produced during the event is shown in Fig. 6 for three cases; a 50% branching ratio for $\text{N}(^2\text{D})$ production for reactions (2) and (3) (Model A), an 80% branching ratio (Model B), and the assumption that each odd nitrogen produced is in the form NO (Model C). The last assumption produces 1.3 NO molecules for each ion pair created during the event. The difference between the curves arises from the increasing

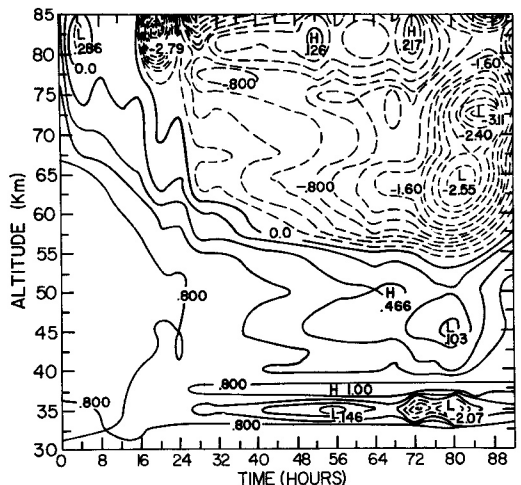


FIG. 5. CONTOURS OF THE EFFICIENCY OF ODD NITROGEN PRODUCTION FOR THE AUGUST 1972 EVENT.

Dashed lines indicate negative efficiency.

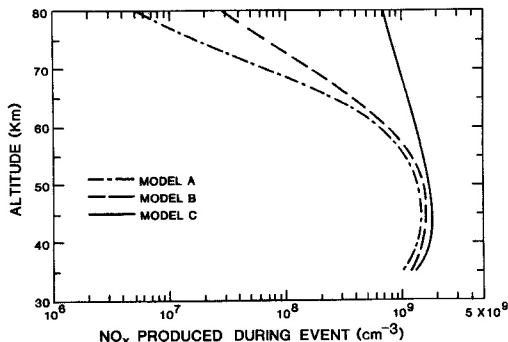


FIG. 6. THE TOTAL AMOUNT OF NO_x PRODUCED DURING THE 1972 EVENT FOR 1.3 NITRIC OXIDE MOLECULES PER ION PAIR (—) (MODEL C), A BRANCHING RATIO OF 50% (— · —) (MODEL A), A BRANCHING RATIO OF 80% (---) (MODEL B).

importance of $\text{N}(\text{S})$ destruction of NO as the branching to $\text{N}(\text{D})$ decreases. For altitudes below 50 km the percentage difference in odd nitrogen produced under the assumption of 1.3 NO molecules per ionization and the assumption of a 50% efficiency is 20%. The divergence of the curves at higher altitudes is due to the rapid saturation of nitric oxide at these levels compared to the total length of the event and the different saturation values resulting from the assumptions in each model.

Clearly the assumption which equates odd nitrogen production to NO production is incorrect and below 60 km the different assumptions still produce a 20% effect on the NO_x production. It should be noted, however, that these effects will be less important for an event at the dark pole. At night, NO is converted to NO_2 by reaction with ozone, and then to NO_3 and N_2O_5 . The conversion from NO to NO_2 occurs rapidly below 50 km. Since the reaction of NO_2 with $\text{N}(\text{S})$ is slower than that of NO with $\text{N}(\text{S})$, the NO_x loss is less effective at night and the efficiencies will increase. Also, it is in these lower regions where odd nitrogen is primarily responsible for the destruction of odd oxygen during proton events.

The calculated per cent ozone reduction for our Models A and B, Model D of Solomon and Crutzen (1980) and a model based on the assumption of 1.5 nitric oxide molecules formed per ion pair are displayed in Fig. 7 along with the revised BUV data of Heath *et al.* (1977) (R. Stolarski, private communication). The calculation of Solomon and Crutzen (1980) adopted an integrated ionization rate somewhat larger than those used here and assumed 1.5 NO molecules/ionization. The results of using

the smaller ionization rate with the same assumption on NO production can be seen by comparing the appropriate curves. The comparison of the calculated and measured ozone depletions are reasonable for both Models A and B. It is, however, difficult to choose between them on the basis of this comparison.

In Table 2 we summarize the results of five model calculations with different assumptions concerning the number of odd nitrogen atoms produced per ion pair, the branching ratio to $\text{N}(\text{D})$, and reaction rate coefficients along with the experimental results labelled b.u.v. The efficiency (E) for the entire event and the per cent ozone change after 8 days are listed for each model. Models A, B, and C represented in Fig. 6 are listed along with two additional calculations. We note that the calculated reduction of O_3 is 10% less in Model A than Model C at 40 km due to the decrease in net NO_x production. Model E incorporates the reaction rate coefficient of Wilson (1967) for reaction (11). The change in the rate from the value of Model A at

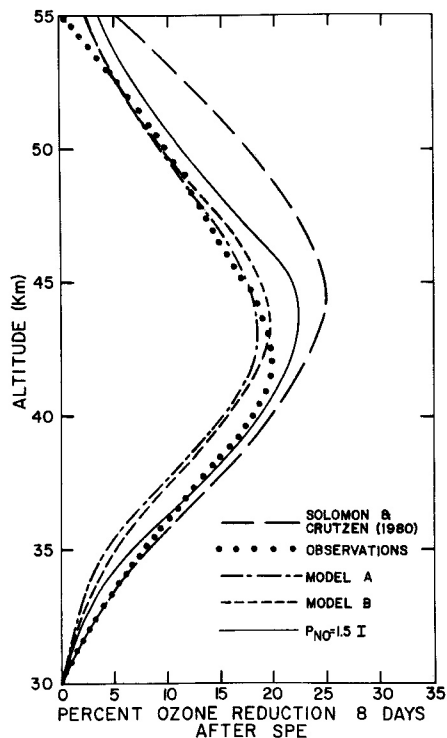


FIG. 7. THE PER CENT OZONE DEPLETION CALCULATED 8 DAYS FROM THE BEGINNING OF THE EVENT COMPARED WITH THE DATA.

Also shown is Model D from Solomon and Crutzen (1980). The curve labeled $P_{\text{NO}} = 1.5I$ is described in the text.

TABLE 2. AVERAGE EFFICIENCY FOR NO PRODUCTION AND CALCULATED OZONE REDUCTION AUGUST, 1972 SOLAR PROTON EVENT

z (km)	b.u.v. % O ₃	Model									
		A		B		C		D		E	
		E	% O ₃	E	% O ₃	E	% O ₃	E	% O ₃	E	% O ₃
30	0	0.98	0	1.0	—	1.00	—	0.86	—	0.58	—
40	18	0.79	14.7	0.87	15.6	1.00	16.6	0.75	18	0.57	11.6
50	10	0.85	8.8	0.90	9.3	1.00	9.8	0.84	12	0.73	7.3
60	0	0.5	0	0.61	—	1.00	—	0.52	3	0.34	—
70	—	0.076	—	0.20	—	1.00	—	0.07	—	0.05	—
80	—	0.005	—	0.063	—	1.00	—	0.014	—	0.006	—

A. NASA Rates,* 50% branching to N(²D), 1.3 NO_x/ionization.

B. NASA Rates,* 80% branching to N(²D), 1.3 NO_x/ionization.

C. NASA Rates,* NO production equal to 1.3 times ionization rate.

D. NASA Rates,* 50% branching to N(²D), 1.62 NO_x/ionization.

E. $k_{N+O_2} = 2.4 \times 10^{-11} \exp(-3975/T)$, 50% branching to N(²D), 1.3 NO_x/ionization.

* Rates for N+NO and N+O₂ adopted from: Chemical kinetic and photochemical data for use in stratospheric modelling: evaluation number 2, NASA Panel for Data Evaluation, Jet Propulsion Laboratory, Publication No. 79-27.

low temperatures significantly affects the total NO_x production as N(⁴S) is a less efficient source of NO in Model A than in Model E. This results in increased NO_x destruction in Model E and less ozone depletion. Model D uses the cross-section of Zipf and McLaughlin to calculate the production of nitrogen atoms. The result of 1.62 nitrogen atoms per ionization increases the total NO_x production by the ratio 1.6/1.3 compared with Model A with a corresponding increase in the ozone destruction. The calculated ozone depletion for Model D agrees closely with the measurements at low altitudes but disagrees sharply at high altitudes.

From the results listed in Table 2 it is difficult to choose the model which most represents the real situation, although we favor Model B because of the arguments presented for the calculated NO_x per ion pair and the calculated ozone loss fits the revised measurements well. The complexities of the comparison and the relatively small differences between the different models compared to the measurement error makes a definitive selection difficult.

DISCUSSION

We have presented calculations of the time-dependent odd nitrogen concentrations in the middle atmosphere subject to proton bombardment and the resulting ozone depletion. A production of 1.3 odd nitrogens per ion pair, an 80% branching ratio for the production of N(²D) by the primary reactions dissociating N₂, and inclusion of the loss of NO_x through N+NO in a time-dependent calculation appears to produce an ozone destruction most compatible with the measurements.

It is apparent from the calculations that the loss of NO by its reaction with N cannot be neglected and that the assumption of a nitric oxide production rate normalized to the ionization rate is invalid. Further, large differences occur between the odd nitrogen production per ion pair in the lower mesosphere-stratosphere and the thermosphere due primarily to the absence or presence of atomic oxygen. In the middle atmosphere, reactions (6) and (7) play no appreciable role in the nitrogen production as N₂⁺ is lost primarily through charge exchange with O₂. In the thermosphere, each N₂⁺ ion formed is capable of producing 2 atomic nitrogen atoms, one through reaction (6) and one through reaction (10). The production of N atoms per ion pair may increase to 3.3 in the lower thermosphere from 1.3 in the middle atmosphere. Thus caution must be exercised when using thermospheric measurements and attempting to apply the results directly to SPE events in the stratosphere.

The efficiency with which odd nitrogen is created during an event is seen to vary in altitude and time, with saturation occurring rapidly at high altitudes and never occurring at low altitudes for the 1972 event.

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REFERENCES

- Bauer, E. A. (1979). *J. geophys. Res.* **84**, 6929.
- Crutzen, P. J. (1970). *J. P. met. Soc.* **96**, 320.
- Crutzen, P. J., Isaksen, I. S. A. and McAfee, J. R. (1978). *J. geophys. Res.* **83**, 345.
- Crutzen, P. J., Isaksen, I. S. A. and Reid, G. C. (1975). *Science* **189**, 457.
- Crutzen, P. J. and Solomon, S. (1981). *Planet. Space Sci.* **28**, 1147.
- Donahue, T. M., Zipf, E. C. and Parkinson, T. D. (1970). *Planet Space Sci.* **18**, 171.
- Fabian, P., Pyle, J. A. and Wells, R. J. (1979). *Nature, Lond.* **277**, 458.
- Frederick, J. C. (1976). *J. geophys. Res.* **81**, 3179.
- Gérard, J.-C. and Barth, C. A. (1977). *J. geophys. Res.* **82**, 674.
- Gérard, J.-C. and Rusch, D. W. (1979). *J. geophys. Res.* **84**, 4335.
- Heath, D. F., Krueger, O. J. and Crutzen, P. J. (1977). *Science* **197**, 886.
- Hyman, E., Strickland, D. J. Julienne, P. S. and Strobel, D. F. (1976). *J. geophys. Res.* **81**, 4765.
- Kieffer, L. J. and Dunn, G. H. (1966). *Rev. Mod. Phys.* **38**, 1.
- Kley, D., Lawrence, G. M. and Stone, E. J. (1977). *J. chem. Phys.* **66**, 4157.
- Narcisi, R. S. and Swider, W. (1976). *J. geophys. Res.* **81**, 4770.
- Niehaus, A. (1967). *Z. Naturf.* **22a**, 690.
- Porter, H. S., Jackman, C. H. and Green, A. E. S. (1976). *J. chem. Phys.* **65**, 154.
- Rapp, D., Briglin, D. D. and Goldan, P. (1965). *J. chem. Phys.* **42**, 4081.
- Reagan, J. B., Gunton, R. C., Evans, J. E., Nightingale, R. W., Johnson, R. G., Imhof, W. L. and Meyerott, R. G. (1978). Lockheed Rep. D630455.
- Reid, G. C., Isaksen, I. S. A., Holzer, T. E. and Crutzen, P. J. (1976). *Nature, Lond.* **259**, 177.
- Roble, R. G. and Gary, J. M. (1979). *Geophys. Res. L.* **6**, 703.
- Roble, R. G. and Rees, M. H. (1977). *Planet. Space Sci.* **25**, 991.
- Rusch, D. W. and Barth, C. A. (1975). *J. geophys. Res.* **80**, 3719.
- Rusch, D. W. and Gérard, J.-C. (1980). *J. geophys. Res.* **85**, 1285.
- Sharp, W. E. (1978). *J. geophys. Res.* **83**, 4373.
- Sharp, W. E., Rees, M. H. and Stewart, A. I. (1979). *J. geophys. Res.* **84**, 1977.
- Solomon, S. and Crutzen, P. J. (1981). *J. geophys. Res.* **86**, 1140.
- Swider, W. and Narcisi, R. S. (1977). *Planet. Space Sci.* **25**, 103.
- Thorne, R. M. (1980). *Pure appl. Geophys.* **118**, 128.
- Vallance Jones, A. (1975). *Can. J. Phys.* **53**, 2267, 2284.
- Weeks, L. H., Cuikey, R. S. and Corbin, J. R. (1972). *J. Atmos. Sci.* **29**, 1138.
- Wilson, W. E. (1967). *J. chem. Phys.* **46**, 2017.
- Winters, H. F. (1966). *J. chem. Phys.* **44**, 1492.
- Zipf, E. C., Espy, P. J. and Boyle, C. F. (1980). *J. geophys. Res.* **85**, 687.
- Zipf, E. C. and McLaughlin, R. W. (1978). *Planet. Space Sci.* **26**, 449.

