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# Reply

J. E. FREDERICK, C. H. JACKMAN, AND R. S. STOLARSKI

*Laboratory for Planetary Atmospheres, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771*

Our goal in *Jackman et al.* [1980] was to evaluate the magnitudes of various proposed sources of odd nitrogen, ON, so they could be compared with each other and especially with the major accepted source in the stratosphere, the oxidation of $N_2O$. In doing this we chose to use measurements wherever possible. For instance, for the production via $O(^1D) + N_2O \rightarrow NO + NO$ we chose to use measured values of $N_2O$ and $O_3$, the latter being needed to compute $O(^1D)$. Thus the results are not totally model-independent. A detailed photochemical model necessarily involves many input parameters whose individual uncertainties combine to produce larger potential errors in the final result. In model studies the goal is self-consistency and achieving the proper coupled response to variations in input parameters; measured profiles are similar to but not the same as those obtained in such calculations. We believe that, for our purpose, the approach based on measurements is preferable to chemical modeling when an adequate trace gas data base exists, as is the case with $N_2O$ and $O_3$.

Self-consistent stratospheric models do provide estimates of the globally averaged ON production rate, and in recent years, as our knowledge of the input quantities required in these calculations has improved, these estimates have changed. *Ellsaesser* [this issue] has selected model estimates of the ON production rate for his Table 1 which are strongly biased toward the early calculations. With the exception of the model value quoted in *Hudson and Reed* [1979], the ON production rates listed by *Ellsaesser* [this issue] are derived from photochemical calculations that have been obsolete for several years. The improvements made in model inputs over the last decade are well known and generally appreciated by the aeronomy community, and, hence, we did not feel it necessary to review results that should be widely recognized as outdated. The difficulty in obtaining a good historical picture of the estimates is that the ON production rate is frequently not quoted from among the many possible diagnostics available to the authors to describe and interpret their results. Actually, the model results quoted by Ellsaesser appear to be taken not from the original papers, but from *Ackerman* [1975]. Many of the original papers do not state the ON production rates explicitly. The next few paragraphs provide a brief review of the sources of the numbers given in Ellsaesser's Table 1.

*Brasseur and Nicolet* [1973] did not give details concerning their calculation of the $N_2O$ profile used to evaluate ON production rates, but instead referred to the work by *Nicolet and Peetermans* [1972]. This earlier paper derives a production rate in the range $(1.5 \pm 1) \times 10^8$ cm$^{-2}$ s$^{-1}$ depending on assumptions made concerning the eddy diffusion coefficient and the solar zenith angle. It is not clear whether this is an appropriate diurnal average or a daylight value only. The abstract of this paper lists a smaller value, $(1 \pm 0.5) \times 10^8$ cm$^{-2}$ s$^{-1}$, which is consistent with numbers one can infer from Figure 24 of *Brasseur and Nicolet* [1973] based on the calculated downward flux of $HNO_3$ at the tropopause. Table 1 of *Brasseur and Nicolet* [1973] gives their calculated altitude profiles of ON production for differing diffusion coefficients and $O(^1D)$ concentrations. These range from 0.5 to $1.9 \times 10^8$ cm$^{-2}$ s$^{-1}$. A problem with this and all of the earlier works was the use of a dissociation rate for $N_2O$ based on cross sections chosen by *Bates and Hays* [1967] which are now recognized as being too large at the longest wavelengths [*Johnston and Selwyn*, 1975]. In addition, the quenching rate of $O(^1D)$ was taken as $5 \times 10^{-11}$ cm$^{-3}$ s$^{-1}$, which is substantially larger than values accepted today [*Hudson and Reed*, 1979] and leads to an underestimate of the metastable atom concentration. The uncertainties that were already appreciated in 1972 led *Nicolet and Peetermans* [1972] to state that one could not put great confidence in model predictions at that time. The problems identified since then further amplify this statement.

Similar comments apply to the input data used in all of the early results listed by Ellsaesser. *Isaksen* [1973] explicitly stated an ON production rate in the range $(0.8 - 1.0) \times 10^8$ cm$^{-2}$ s$^{-1}$. However, he stressed the great sensitivity of the computed $N_2O$ abundances to the adopted eddy diffusion coefficients, noting that his calculations predict a mixing ratio decrease by nearly 2 orders of magnitude between the tropopause and 35 km. *Crutzen* [1974] did not give an integrated ON production rate; however, his earlier work [*Crutzen*, 1971] yielded values in the range $(0.29 - 0.5) \times 10^8$ cm$^{-2}$ s$^{-1}$. These results are based on altitude independent diffusion coefficients of $10^3$ and $10^4$ cm$^2$ s$^{-1}$, respectively, which are very different from values in use today. In addition, the $N_2O$ volume mixing ratio of $2.5 \times 10^{-7}$ assumed at the tropopause is smaller than now accepted. *Wofsy and McElroy* [1974] did not give the values attributed to them in Ellsaesser's Table 1, although these results were published in *McElroy and McConnell* [1971]. Once again, the numbers are sensitive to model inputs whose accepted values have changed over the last decade. The model results which Ellsaesser quotes as *Ackerman* [1975] are merely the extremes of the values given in the references discussed above and do not represent an independent examination of the problem.

We conclude that none of the ON production rates referenced by Ellsaesser are acceptable today, except for the result in *Hudson and Reed* [1979] that is based on more recent model inputs. This in no way detracts from the usefulness of the older studies when viewed in their proper context, namely, as preliminary attempts to examine the odd nitrogen budget by using the input data available in the early 1970's.

The ON production rates that Ellsaesser refers to as 'from observations' involve some degree of modeling since $O(^1D)$ must be computed or characteristic times for stratosphere-troposphere air exchange must be considered. The large production rate deduced by *Schmeltekopf et al.* [1977], $4.5 \times 10^8$ cm$^{-2}$ s$^{-1}$, used $O(^1D)$ computed from the two-dimensional



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model of P. J. Crutzen. This suggests that the ozone that produces $O(^1D)$ was also computed. If this is true, then some degree of model uncertainty enters the results. In any case, *Johnston et al.* [1979] stated that differences in the extrapolation of measured $N_2O$ profiles to higher altitudes may account for much of the difference between his result, $2.8 \times 10^8$ cm$^{-2}$ s$^{-1}$, and that of *Schmeltekopf et al.* [1977]. The value given in *Hudson and Reed* [1979] is simply a reference to the *Schmeltekopf et al.* [1977] result and was not an independent calculation. Finally, the wide spread quoted by *Ackerman* [1975], $0.8 - 5.0 \times 10^8$ cm$^{-2}$ s$^{-1}$, encompasses the results of *Schmeltekopf et al.* [1977], *Johnston et al.* [1979], and *Jackman et al.* [1980]; however, details of how this range was obtained from $HNO_3$ measurements were not given.

To assess the current comparison between self-consistent one-dimensional (1-D) calculations and two-dimensional determinations based on data, we have performed two calculations of the globally averaged ON production rate, using the latest version of the 1-D model first described by *Rundel et al.* [1978] and *Stolarski et al.* [1978]. The initial test used the most recent inputs available and includes currently accepted $N_2O$ cross sections, $O(^1D)$ quenching rates [*Hudson and Reed*, 1979], and NO dissociation rates [*Frederick and Hudson*, 1979]. The second calculation uses most of these same inputs except that it is more like calculations in the older references quoted by *Ellsaesser* [this issue] in that loss of ON via NO dissociation and $N + NO \rightarrow N_2 + O$ is neglected and $J(N_2O)$ extends to wavelengths around 330 nm. The currently accepted chemistry predicts an ON production rate of $2.5 \times 10^8$ cm$^{-2}$ s$^{-1}$ and a maximum mixing ratio of 23 ppbv. The older model inputs produce corresponding values of $1.0 \times 10^8$ cm$^{-2}$ s$^{-1}$ and 12 ppbv. We note that the most recent value of the $O(^1D) + N_2O$ reaction rate is $7.2 \times 10^{-11}$ cm$^3$ s$^{-1}$ with a possible error of ±40% [*NASA Panel*, 1981] as compared to $5.5 \times 10^{-11}$ cm$^3$ s$^{-1}$ available when the *Jackman et al.* [1980] work was completed. Hence, the *Jackman et al.* [1980] result should be increased from $2.8 \times 10^8$ cm$^{-2}$ s$^{-1}$ to $3.7 \times 10^8$ cm$^{-2}$ s$^{-1}$. The ratio of this updated empirical value to that computed from the latest model inputs is 1.5. In view of the uncertainties that likely remain in theoretical calculations, we cannot regard this as a major discrepancy. Perhaps the more interesting aspect is that the currently accepted rates yield ON concentrations somewhat higher than the measurements [*Hudson and Reed*, 1979] while giving integrated production rates somewhat lower than those deduced from measured $N_2O$ and $O_3$. This discrepancy is suggestive that some changes will continue to be made in our understanding of the stratospheric odd nitrogen budget. It is not at all certain, however, that the changes will be more than minor adjustments, as the discrepancies are still within the stated uncertainty estimates.

A further concern implicit in Ellsaesser's comment concerns the computed effects of artificial injections of ON such as by high flying aircraft. We simulated an injection of $1 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$ at 20 km in both versions of the model described above. The current input data gave a column ozone change of 2.3% while the modified data set (i.e., no ON sink via $N + NO$ and $J(N_2O)$ extending to 330 nm) yielded 2.1%. Thus the factor of 2.5 change in the computed ON production rate had little effect on the ozone perturbation.

In conclusion, we agree with Ellsaesser that recognition of discrepancies between model results and measurements can be a first step toward new discoveries. However, such comparisons must be performed with an adequate understanding of the limitations in both the calculations and data in order to be of service to the scientific community.

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