CONFERENCE ON THE UPPER ATMOSPHERE

A portion of the contents of this issue of the Journal of the Atmospheric Sciences is devoted to studies of our upper atmosphere—the stratosphere, mesosphere, and thermosphere. Most of these papers, but not all, are based on presentations in more or less similar form made at the Conference on the Upper Atmosphere, 30 September–4 October 1974, in Atlanta, Ga., organized by the Committee on the Upper Atmosphere of the American Meteorological Society.

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NO, NO₂ and HNO₃ below 35 km in the Atmosphere

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ABSTRACT

Experimental data on NO, NO₂ and HNO₃ in the atmosphere are reviewed. The low abundance of nitric acid in the tropospheric gas phase is emphasized, as well as the high variability of NO₂ in the low stratosphere and in the troposphere. Some model-predicted distributions of these odd-nitrogen molecules are presented. Areas of agreement and of disagreement between theory and experiment are indicated.

1. Introduction

Stratospheric research has remained rather academic until recently. In 1971 it was assumed (Johnston, 1971) that the projected increase in the oxides of nitrogen from aircraft flying in the stratosphere could reduce the ozone shield by about a factor of 2, thus permitting increased ultraviolet radiation below 300 nm to reach the lower atmosphere, and consequently endanger life at the earth surface. The interest of aircraft industries and governmental agencies in the problem has changed the level of activity in stratospheric research. Increased emphasis has been put on measuring and modeling the natural stratosphere in order to be able to predict possible modifications.

Ozone is formed from atomic oxygen resulting from the dissociation of molecular oxygen by solar ultraviolet radiation:

\[ O_2 + h\nu \rightarrow O + O \]  \hspace{1cm} (1)

Ozone reduction would result in more scavenging of odd-oxygen atoms in a catalytic set of reactions involving increased nitric oxide and nitrogen dioxide:

\[ NO_2 + O \rightarrow NO + O_2 \]  \hspace{1cm} (3)

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  \hspace{1cm} (4)

It is currently accepted that nitric oxide is formed in the stratosphere by reaction of nitrous oxide originating from biological activity at ground level. Since odd-nitrogen molecules have not continued to build up, a removal mechanism has been suggested, based on nitric acid rainout.

Three years of experimental work have yielded only preliminary knowledge of the real natural abundance of NO, NO₂ and HNO₃ in the stratosphere. It is time to summarize the available results and to compare them with theoretical predictions.
NO can only be conjectured. Its abundance is known, however, to vary with time and location (Ackerman et al., 1974; Ridley et al., 1974; Savage et al., 1974).

The nitric oxide observations made at 19 km by Savage et al. (1974) over the period from November 1973 to June 1974 from 75° to 120°W and from 33° to 49°N indicate an NO concentration increase of a factor of 7, reaching a value of $1.4 \times 10^6$ cm$^{-3}$ which persisted until the end of May. This was most probably due to horizontal transport by air motion since the variation is too large to be accounted for by ozone fluctuations that would change the NO$_2$/NO ratio by reactions (4) and (5). It is thus not surprising to find two vertical distributions (see Fig. 1), each observed (Ackerman et al., 1974) with the same instrumentation under the same experimental conditions but separated by almost exactly one year, which exhibit a difference of a factor of 2–10 at 24 km. The meteorological situations shown in Figs. 2a and 2b were quite different for the two observations, each at 44°N, 1°–3°W. The surface synoptic maps were rather typical for the period preceding the experiments, with low pressures reaching lower latitudes in May 1974 than in May 1973. It might also be interesting to notice (see Figs. 3a and 3b) that the soundings made over Arosa showed that the ozone layer below the peak changed significantly from the period of the first experiment (9–16 May 1973) to that of the second (8–17 May 1974). Tropospheric air was clearly being injected into the stratosphere in the second case from 10 to 18 km; in addition there was a marked layer of variability from 22 to 28 km.

However there are too few measurements of nitric oxide at present to attempt quantitative evaluations of the observed variations. Their interpretation obviously requires the simultaneous observation of several parameters including minor constituents and dynamic processes on a synoptic basis of reasonable extent.

3. Nitrogen dioxide

Observations of available nitrogen dioxide number densities for the troposphere and for the stratosphere are plotted in Fig. 4. Chemical analysis (Moore, 1974; Nash, 1974; Georgii and Jost, 1964) of air samples from ground level up to 6 km and remote spectrometry (Brewer et al., 1973) have been used in the troposphere to determine NO$_2$. The experimental values are spread over almost two orders of magnitude. Measurements of supposed unpolluted ground level air indicate values that could differ by factors of more than 100. Georgii and Jost (1964) conclude from their aircraft measurements that tropospheric NO$_2$ originates partly from biological activity in soils; the latter source would explain why values observed in summer are higher than those observed in winter. The observed enrichment in NO$_2$ (Moore, 1974) for tropospheric NO$_2$ could be due to the biological contribution. An important variability of tropospheric NO$_2$ seems to be firmly

2. Nitric oxide

Detection of nitric oxide in the stratosphere has been reported by various authors (Toth et al., 1973; Ridley et al., 1973; Girard et al., 1973). Vertical distributions of this constituent have been derived by absorption spectrometry using the sun as a source (Ackerman et al., 1973, 1974) and by chemiluminescence with O$_2$ (Ridley et al., 1974). After sunset, reaction (4) should transform nitric oxide that has been observed (Patel et al., 1974) to appear after sunrise by the photodissociation process

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}_2,$$  

(regenerating atomic oxygen available for ozone formation by reaction (2)). Chemiluminescence has also been used on high-flying aircraft (Lowenstein et al., 1974) to measure stratospheric NO. This method indicates large variations at 18 and 20 km over a period of several months (Savage et al., 1974).

Nitric oxide has also been determined in the mesosphere and in the lower thermosphere.

Most of the experimental data are illustrated in Fig. 1. They indicate higher number densities in the stratosphere than in the mesosphere, suggesting different production regimes as postulated on theoretical grounds (Nicolet, 1971). A steep decrease is observed below 30 km and possibly an increase in the vicinity of the tropopause below which no observations are available.

Most of the measurements have been obtained at mid-latitudes so that the possible meridional variation of...
FIG. 2. Surface pressure maps for the two dates of the NO measurements reported by Ackerman et al. (1974). Low pressures were extending toward lower latitudes on 14 May, 1974 (Fig. 2a) than in the case of 13 May 1973 (Fig. 2b). These situations were rather characteristic of the two periods.
Fig. 3. Height profiles of ozone partial pressure over Switzerland for the two NO observation periods (Ackerman et al., 1974). In 1973 ozone appears to vary from day to day at random, while in 1974 a trend is observed below 18 km; an organized decrease occurs from 8 to 17 May.

established as well as the influence of human activities. Robinson and Robins (1971) propose a latitudinal variation (4 ppb over tropic and temperate land areas, 0.5 ppb over polar land areas and oceans).

The abundance of NO2 in the stratosphere is known from infrared remote spectrometry (Ackerman and Muller, 1972, 1973; Farmer, 1974; Ackerman et al., 1974; Fontanella et al., 1974) performed from balloon gondolas and from aircraft. As is the case for NO, the few available determinations are also at mid-latitudes limiting the possible comparison with theoretical models to roughly 45°N which could be representative of average conditions.

Several models have yielded NO and NO2 vertical distributions for average conditions and even for specific latitudes and seasons. Some of the results are illustrated in Fig. 5. Models where various sets of

Fig. 4. Height profiles of nitrogen dioxide number densities measured by means of ground-based, aircraft and balloon-borne instruments. Constant volume mixing ratios are roughly indicated by the straight lines marked $10^{-3}, 10^{-9}$ and $10^{-10}$.

possible vertical distributions are proposed can hardly be compared with experimental results. In one case represented in Fig. 5 (Levy, 1973) a tropospheric abundance of NO2 was assumed to be due to the effect of other parameters. Modeling data are consistent with each other and with experimental results at 30 km altitude; the situation is different, however, at lower altitudes. It should be pointed out that the various

Fig. 5. Theoretically evaluated NO2 number densities versus altitude, where only models yielding unique distributions have been used. When various latitudes have been considered, values for 45° latitude are represented. Levy (1973) did not compute NO2 but introduced a distribution to compute other parameters. Constant volume mixing ratios are represented by straight lines marked $10^{-3}, 10^{-9}$ and $10^{-10}$. 
models considered give NO$_2$ values at 30 km that agree within a factor of 2, while values at 15 km are spread over a factor of 20. Does this mean a weak coupling between the two altitudes? Particularly in the tropopause region, values deduced in models are spread over two orders of magnitude even if it does not seem to have been the authors' intention to represent such variability aspects. Models can produce double and single peaks in the vertical distributions, but only the latter situation has been observed.

Due to the short characteristic time (~100 s) for converting NO to NO$_2$ and NO$_2$ to NO in daylight through reactions (4), (5) and (3), the latter being negligible in the low stratosphere, the balance of these two oxides of nitrogen can better be represented by their sum, currently called NO$_x$. This can be evaluated from experimental NO$_2$ and NO data available from ground level up to 36 km by

\[ \text{NO}_2 = \text{NO}_x \left( \frac{1+R}{R} \right) = \text{NO} (1+R), \]

where

\[ R = \frac{k_d[O_3]}{J_1 + k_d[O_3]} \]

The ratio $R$ has been evaluated by several authors, and measured once—results are shown as altitude profiles in Fig. 6. From the curve given by Brasier and Nicolet (1973) which best represents the experimental data at the altitudes where comparison is possible, and from the NO$_2$ and NO measurements shown in Fig. 1 and in Fig. 4, a possible envelope of NO$_2$ values has been evaluated and is given in Fig. 7. It will be discussed later.

4. Nitric acid

Absorption spectra have led to the detection (Murray et al., 1968) of HNO$_3$ in the stratosphere and to several determinations. A rather large number of measurements make this odd nitrogen molecule the most measured in the stratosphere of the three that are considered here. High-resolution absorption spectroscopy performed from ground level (Vigroux, 1973) has indicated on the basis of the narrowness of the observed lines that HNO$_3$ is more abundant in the upper than in the lower layers of the atmosphere. Aircraft emission spectroscopy (Harries et al., 1974) has revealed a sharp increase of nitric acid above the tropopause. The same method at shorter wavelengths on balloon gondolas (Murray et al., 1974) has yielded vertical distributions of the abundance of nitric acid in the stratosphere at various latitudes. The chemical analysis of in situ collected samples (Lazrus and Gandel, 1974) has also demonstrated the variability of nitric acid with time and latitude with higher values toward the pole than toward the equator. The results obtained by this method tend to be the lowest, particularly at low altitudes, while absorption spectroscopy from aircraft (Fontanella et al., 1974) has a tendency to give the highest concentrations as well as some interpretations of emission measurements (Fried and Weinman, 1970).

No optical measurement seems to have been reported for HNO$_3$ in the troposphere. We have used spectra taken by absorption spectrometry during balloon ascents and published by Murray et al. (1969) to evaluate one tropospheric upper limit corresponding to a volume mixing ratio less than 10$^{-10}$. The result is shown in Fig. 8 with envelopes representing the data obtained by means of the various methods at various times and locations. All results are included in the broad envelope illustrated in Fig. 7.
Fig. 8. Envelopes representing the measured height profiles of nitric acid number densities. L-G corresponds to the data of Lazarus and Gandrud (1974), M to those of Murgray et al. (1974), G to those of Fontanella et al. (1974), W to those of Fried and Weinman (1970), and H to those of Harries et al. (1974). The values represented by the circles and by the upper limit marked T have been evaluated on the basis of the atmospheric experiments of Murgray et al. (1969) and of the laboratory data published by Fontanella et al. (1974). Constant volume mixing ratios are roughly illustrated by the straight lines marked $10^{-9}$, $10^{-8}$ and $10^{-10}$.

Examples of theoretically deduced vertical distributions of HNO₃ are shown in Fig. 9. Values for altitudes higher than 15 km are in good agreement with observations while below 12 km, the theory appears to give HNO₃ abundances which are too high.

5. Discussion

Nitric acid, like other very polar molecules such as HCl, is known to have an extremely low activity in dilute aqueous solutions. On the other hand, Warneck (1974) has shown that the time constant for collisions of trace constituents with cloud elements is shorter than 5 s. These considerations would explain a low concentration of HNO₃ in the tropospheric gas phase. They have not been taken into account in models where rain-out times of the order of a few days have been introduced to represent the evacuation of odd nitrogen from the stratosphere to the troposphere. They would, however, possibly improve agreement between theory and experiment in the region of the tropopause and below. This would probably require adjustments to maintain the computed concentrations of NO₂ at the level indicated by the observations requiring other sources of odd nitrogen in the low stratosphere.

There is obviously an important time variability of NO in the stratosphere. Seasonal variations have been considered in models as well as the possibility (Ruderman and Chamberlain, 1974) of interpreting the apparent correlation of ozone variation with the 11-year cycle of solar activity in terms of the effect of nitrogen oxide modulation by cosmic rays. Even if doubts have been cast on the significance of such correlations (London and Oltrmans, 1973), such investigations are very interesting. There is, however, no convincing demonstration of the possible direct role of nitrogen oxides as an intermediate agent in these phenomena that would allow us to make firm assessments now (Johnston, 1974) about the possible effects of stratospheric aircraft on ozone. As noted earlier, large variations of NO have been observed. The NO abundances observed by Ackerman et al. in May of 1973 and 1974 differ markedly. Total ozone data for the two months are shown in Fig. 10. In May 1973, total ozone appears to vary from day to day randomly around mean values larger at high latitudes than currently observed. The latitudinal variation is also present in May 1974, but a well-pronounced decrease of 10–20% appears over one week. The observations indicate the occurrence of a well-organized modification of large geographic extent from at least 51° to 39°N, including the area of high NO observations. It is suggested that the decrease in total ozone is due to the replacement of ozone-rich air below 20 km by ozone-poor air. This suggestion stems from the observed vertical profiles observed over Switzerland and shown in Fig. 3a and 3b. Umkehr observations made over Lisbon near the end of the ozone spring maximum at this station (Figueira, 1973) and at other times during the year show the same trend, namely, during the minimum of total ozone in the month of May 1974, levels 2 and 3 (12 and 16.5 km) exhibit minimum values while maximum values for the whole month are observed at levels 5, 6 and 7 (25, 30 and 35 km).

The ozone reduction below 20 km responsible for the reduction in total ozone cannot be attributed to NO₃ chemistry since the currently accepted atomic oxygen content at these altitudes implies a characteristic reaction time larger than a year. It should also be remarked.
that an ozone decrease in the lower stratosphere occurred concurrently with an increase at higher altitudes. All these observations suggest that the time variability of total ozone, which could quite simply be related in this case with NO$_x$ on the basis of chemical interactions, was entirely under the control of transport processes.

Determinations of tropospheric NO$_x$ indicate a wide range of NO$_x$ values tentatively illustrated in Fig. 7. Low values are usually thought to be characteristic of unpolluted air and are much smaller than those used in models (Levy, 1973; Chameides and Walker, 1973). The reduction of NO$_x$ in these models would reduce the production of HNO$_3$ that has been considered as being too high by Warner (1974) on the basis of the observed global precipitation of nitric acid in rain. On the other hand, high values of NO$_x$ concentrations, suggested by the observations of Georgii and Jost who have indicated a seasonal variation (summer values higher than those observed in winter) that could hardly be explained on the basis of human activities, could have consequences for the stratosphere. They could lead to injections of tropospheric NO$_x$ into the stratosphere when its mixing ratio at stratospheric heights is smaller than in the troposphere. This could be supported by the isotopic composition of HNO$_3$ observed between 21 and 27 km (Moore, 1974) showing about the same N$^{15}$/N$^{16}$ ratio as for standard N$_2$. If stratospheric HNO$_3$ were all derived from N$_2$O that shows a marked N$^{18}$ enrichment, this should also appear in nitric acid as a product of NO$_x$, provided that reactions

$$N_2O + O^1D \rightarrow N_2 + O_2 \quad \text{(6)}$$

$$N_2O + O^1D \rightarrow NO + NO \quad \text{(7)}$$

have no differential isotopic effects. This could be a reasonable assumption that should of course be checked to allow a definite interpretation of the stratospheric isotopic measurements.

If we consider the replacement time (Danielsen 1968) of stratospheric air by tropospheric air and the high HNO$_3$ amounts derived by absorption spectrometry (Fontanella et al., 1974), we arrive at a downward flux of nitric acid larger than 5 x 10$^8$ cm$^{-2}$ s$^{-1}$. This would imply that a source of odd stratospheric nitrogen other than that from (7) has led to the odd nitrogen productions of (0.29–1.5) x 10$^8$, (0.25–0.65) x 10$^8$, (0.5–1.3) x 10$^8$ and (0.8–1.0) x 10$^8$ cm$^{-2}$ s$^{-1}$, respectively, proposed by Crutzen (1974), Wofsy and McElroy (1974), Brasseur and Nicolet (1973) and Isaksen (1973).

On the other hand, the low HNO$_3$ values of Fig. 8 would imply, on the basis of the same interchange time between tropospheric and stratospheric air, a flux equal to 0.8 x 10$^8$ cm$^{-2}$ s$^{-1}$. The average value (2.9±2.1) x 10$^8$ cm$^{-2}$ s$^{-1}$ shows clearly that the actual uncertainty of the HNO$_3$ measurements is unsatisfactory. If it was admitted that HNO$_3$ abundances derived from in situ sampling were systematically too low and if, on the basis of such an argument, they were rejected, an average flux value of (3±2) x 10$^8$ cm$^{-2}$ s$^{-1}$ would be derived (excluding several theoretical values). An additional source of odd stratospheric nitrogen would have to be introduced, particularly if a first measurement showed that the absolute quantum yield for the formation of O$^1D$ by the O$_3$ photolysis, the value of which has always been assumed (Welge, 1974), is in fact smaller than currently accepted.

6. Conclusion

Measurements of the chemically related odd nitrogen molecules in the atmosphere appear to be a particularly good test for models designed to predict the possible modifications of the stratosphere under natural and artificial constraints. Measurements are at present too sparse to provide a thorough check. However, they indicate possibilities of improving the evaluation of vertical distributions and temporal variations of NO$_x$. 

Fig. 10. Total ozone versus time measured over various European stations in May 1973 and in May 1974. The beginning of the summer minimum occurs in this latter case while May 1973 is still in the spring maximum.
and HNO₃ particularly required for the lower stratosphere and for the troposphere.

Further investigation is essential if we are to understand such fundamentals as the sources and sinks of odd nitrogen above the average tropopause height and in the troposphere. To date, certain experimental methods have contributed the most to the gathering of the available information, and their use should be intensified; it may also be that others should be reevaluated.

As far as the prediction of a possible reduction of ozone by a factor of 2 is concerned, some models now predict a reduction by only 1% for the same fleet of stratospheric aircraft. And none of the present models can be used for natural stratospheric forecasts.

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