In situ measurements of the NO₂/NO ratio for testing atmospheric photochemical models

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Abstract. Simultaneous in situ measurements of NO₂, NO, O₃, ClO, pressure and temperature have been made for the first time, presenting a unique opportunity to test our current understanding of the photochemistry of the lower stratosphere. Data were collected from several flights of the ER-2 aircraft at mid-latitudes in May 1993 during NASA’s Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE). The daytime ratio of NO₂/NO remains fairly constant at 19 km with a typical value of 0.68 and standard deviation of ± 0.17. The ratio observations are compared with simple steady-state calculations based on laboratory-measured reaction rates and modeled NO₂ photolysis rates. At each measurement point the daytime NO₂/NO with its measurement uncertainty overlap the results of steady-state calculations and associated uncertainty. However, over all the ER-2 flights examined, the model systematically overestimates the ratio by 40% on average. Possible sources of error are examined in both model and measurements. It is shown that more accurate laboratory determinations of the NO + O₃ reaction rate and of the NO₂ cross-sections in the 200-220 K temperature range characteristic of the lower stratosphere would allow for a more robust test of our knowledge of NOₓ photochemistry by reducing significant sources of uncertainties in the interpretation of stratospheric measurements. The present measurements are compared with earlier observations of the ratio at higher altitudes.

Introduction

NO₂ and NO, two major constituents of the nitrogen oxide family in the stratosphere, rapidly interchange during the day through a small set of reactions:

\[
\begin{align*}
\text{NO}_2 + hv & \rightarrow \text{NO} + \text{O} \quad [1] \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad [2] \\
\text{NO} + \text{ClO} & \rightarrow \text{NO}_2 + \text{Cl} \quad [3] \\
\text{NO} + \text{BrO} & \rightarrow \text{NO}_2 + \text{Br} \quad [4] \\
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \quad [5]
\end{align*}
\]

Because of the small timescales associated with these reactions (a few minutes at 20 km down to a few seconds at 30 km), a photochemical steady-state exists between daytime concentrations of NO₂ and NO, and their ratio is approximated by the relationship:

\[
\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_2[\text{O}_3] + k_3[\text{ClO}]}{J_{\text{NO}_2}}
\]

where \(J_{\text{NO}_2}\) is the photodissociation coefficient for NO₂, and the \(k\)'s refer to the temperature-dependent bimolecular rate constants for reactions indicated by the subscripts. In writing equation [6], reactions [4] and [5] are omitted as they account for a negligible fraction of the total NO loss at 20 km. In addition, the reaction of NO₂ with atomic oxygen is also neglected since at the altitudes considered here it contributes less than 0.1% of the total loss of NO₂. NOx (defined here as NO+NO₂) along with odd-hydrogen and odd-chlorine cycles control stratospheric ozone [McElroy et al., 1992].

Previous simultaneous measurements of NO₂ and NO include long-path solar occultation [Louisnard et al., 1983; Russell et al., 1988], long-path limb-scanning radiometry [Drummond et al., 1978; Roscoe et al., 1986], in situ chemiluminescence detection [McFarland et al., 1986; Fabian et al., 1987], and long path tunable diode laser absorption spectroscopy [Webster et al., 1987; Webster et al., 1990]. While observations and model results showed generally good agreement within their combined uncertainties, comparisons were somewhat frustrated by high uncertainties in measurements of NO and NO₂ [McFarland et al., 1986], difficulties in solar occultation retrievals [Allen et al., 1990], or lack of measurements of one or more of the other key variables (ClO, O₃) needed for a complete test of photochemical theory.

The recent addition of new measurement capability for NO₂ to the ER-2 payload in May 1993, combined with simultaneous in situ measurements of NO, O₃, ClO, temperature and pressure, provide a unique opportunity to test our current understanding of NOₓ photochemistry. In this paper we first compare in situ measurements with steady-state predictions as a test of photochemical theory, and then examine the behavior of the ratio as a function of altitude.

The aircraft instruments

The series of flights discussed here were part of SPADE, during the month of May 1993. In flights typically 7-8 hours long, the ER-2 aircraft attains a pressure of about 65 mbar (19 km), covering a maximum latitude range of about ± 22°.

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument, which is a scanning tunable diode laser spectrometer [Webster et al., 1994], measured NO₂, HCl, N₂O and CH₄ using high resolution laser absorption at wavelengths from 3 to 8 μm. While ALIAS measured NO₂ for the first time during SPADE, numerous measurements using a
similar method and laser have been successfully carried out in the past by the Balloon-borne Laser In Situ Sensor (BLISS) instrument [Webster et al., 1987]. Secondary NOx production or loss is not expected during the 1-second transit time through the halocarbon wax-coated inlet. The measurement uncertainty for five-minute averages of NO2 depends on the signal size as well as on uncertainties in spectral parameters and calibration. The total uncertainty is typically 13% at 400 pptv, 17% at 200 pptv, and 25% for the smaller volume mixing ratios around 100 pptv (the corresponding signal to noise ratios varying between 16:1 to 5:1).

NO is measured by a chemiluminescence detector with an estimated accuracy of 20% [Fahey et al., 1993]. C10 is measured by resonance fluorescence with a 15% accuracy [Brune et al., 1988], and O3 by UV absorption [Proffitt et al., 1989] to 5%. All the uncertainties are given as 1σ.

The models

The predicted steady-state values of NO2/NO at the local temperatures and pressures were obtained by combining the measured O3 and C10 in expression [6]. Unless otherwise specified, the temperature-dependent rate constants are from DeMore et al. [1992]. JNO2 is calculated by a radiative transfer model [Salawitch et al., 1994] which uses ozone profiles from the climatology that are scaled to TOMS satellite column ozone measurements, and albedoes derived from TOMS reflectance maps.

Results/Discussion

Daytime NO2/NO ratio

NO2/NO measurements from three flights have been combined in Fig. 1 (open circles) to reconstruct a full sunrise to sunset cycle. The ratio exhibits a remarkable homogeneity between 9 am and 5 pm at a mean value of 0.68 (with a typical standard deviation of ± 0.17), illustrating the relative uniformity of the atmosphere sampled by the ER-2 in May of 1993 during SPADE. Strong midday springtime photolysis of NO2 shifts the steady-state ratio toward NO. Loss of NO is dominated by reaction [2] with ozone, which contributes on average approximately 90% of the total NO loss. Aside from random instrumental uncertainties, the observed variability (≈ 25%) in daytime NO2/NO reflects the transport-driven variability of ozone (≈ 12%), the variability in JNO2 (≈ 10%) caused by the changing tropospheric albedo as the ER-2 plane flies over different types of surfaces and varying cloud cover, and the temperature changes affecting reaction rate k2 (≈ 10%). The individual measurements of NO2 and NO, along with the modeled JNO2 are shown on Fig. 2. At sunset NO is seen to be very rapidly converted to NO2 as visible and ultraviolet light diminishes. It is the dependence of JNO2 on solar zenith angles (SZA) larger than 80° that drives the corresponding rapid increase of the ratio. Symmetrically, during sunrise NO2 is photolysed to form NO.

The calculated algebraic ratios are represented in Fig. 1 as small filled circles. They generally follow the observations, reflecting the validity of the steady-state assumption during daytime. Close to sunset and sunrise the photostationary steady-state assumption no longer applies as the photolysis rate of NO2 changes too rapidly for equilibrium to be established. Although during daytime at each point along the ER-2 flight tracks the uncertainty in the calculated ratio (represented by double headed arrow) is found to overlap the measurement uncertainty, overall the calculated steady-state expression has a clear tendency to overestimate systematically the observed ratio by 40% on average. The significance of this overestimation has been tested using a chi-square test on the difference between model and observations, with a resulting statistical confidence level of 0.01%. Possible sources of this systematic bias, including (1) errors in the rate constants used as input in equation [6]; (2) systematic instrumental bias in the observations, and (3) incomplete knowledge of the NOx chemistry, are considered below.

![Figure 1](image1.png)

**Figure 1.** Comparison of measurements (open circles - error bars every 4 hours) and steady-state predictions (small filled circles with double headed arrows as error bars) of NO2/NO for the SPADE flights of May 6, 7, and 18 1993. Each measurement point is a 5-minute average. The data was selected for pressures below 70 mbar.

![Figure 2](image2.png)

**Figure 2.** ER-2 observations of NO2 and NO for the same flights as Fig. 1; modeled JNO2 used in the steady-state calculations.
Comparison between model and observations: error analysis

The individual error contribution of each input parameter to equation [6] has been calculated following the method of Harries [1982], for conditions typical of the SPADE May flights. The results are summarized in Table 1 along with 1σ uncertainties of observed concentrations, calculated JNO2 and kinetic rate constants based on the temperature-dependent factors listed by DeMore et al. [1992]. The root sum squares show a total uncertainty of 26% in the observed ratio (NO2/NO)obs and of 59% in the calculated steady-state ratio (NO2/NO)ss. In Table 1, k2 and JNO2 can be identified as the key parameters which contribute most to the model's total uncertainty, and thus they are the variables which have most leverage on the calculated ratio within the limit of their 1σ uncertainties, while all the other parameters produce errors of 5% or less. The large uncertainty range of k2 quoted by DeMore et al. especially at the low temperatures (200-220K) of interest here reflects the uncertainties in a given experiment as well as the differences between the various laboratory groups considered.

We have plotted in Fig. 3a the ratio from five SPADE flights as a function of ozone. The linear correlation with ozone is expected because, as seen earlier, k2([O3]) dominates the numerator of the ratio in [6]. The difference in variability between model and observations is due to the superposition of random errors in the measurements of NO and NO2. Although most of the data are contained within the two dotted lines (upper and lower limits on the steady-state calculations), there clearly is a systematic overestimation of the calculated steady-state ratio on Fig. 3a. We can see in Fig. 3b that reasonable changes of the two rates k2 and JNO2 will tend to reconcile the differences between model and measurements. As an illustration, the effect of decreasing k2 by 35% (case 1) is shown on Fig. 3b. A similar very good agreement can also be reached, for example, by decreasing k2 by 25% while increasing JNO2 by 15%. Interestingly, we note that the measurements reported by Ray et al. [1981] are close to the 35% reduction in k2 that is illustrated by case 1.

Simultaneous HO2 measurements during SPADE [Wennberg et al., 1994] have allowed us to check that reaction [4] contributes to about 1% of the total NO loss. Reaction with BrO, the abundances of which are based on the climatology developed by Wennberg et al., accounts for 2% of the loss. Thus including both these reactions would have only slightly increased the calculated ratio.

A systematic underestimation by the radiative transfer model of JNO2 could result in the observed discrepancy. We note that preliminary JNO2 values derived by the Composition and Photodissociative Flux Measurement (CPFM) using a spectrometer aboard the ER-2 seem to suggest an even smaller photolysis rate for NO2 [T. McElroy, personal communication, 1994] leading to an even higher calculated steady-state NO2/NO. Both radiative transfer calculations and CPFM derivations are using NO2 cross-sections and quantum yields recommended by DeMore et al. [1992]. Self-reaction of NO2 and strong temperature dependence of its UV-visible spectrum contribute to difficulties in their laboratory determinations [Roscoe et al., 1993]. Furthermore there are no measurements below 230 K.

The possibility of systematic errors associated with the individual measurements of NO and NO2 themselves has to be considered. To the best of our knowledge, there is no evidence such errors. Furthermore, we note that using independent observations of NO2 by the NOAA instrument [Gao et al., 1994] on the ER-2 flight of May 12 leads to the same overestimation.

Finally, incomplete knowledge of NOx photochemistry cannot be entirely ruled out until more accurate laboratory studies of the rate constants for reactions [1] and [2] at low temperatures are made.

Behavior of the partitioning between NO2 and NO as a function of altitude

Figure 4 displays the daytime ratio measured during the May 1993 flights of SPADE along with previous higher altitude balloon observations (all within a few hours of noon). The value of the NO2/NO ratio is of the order of one in the major
part of the stratosphere. The increase up to about 25-30 km follows the ozone concentration profile, as shown by equation [6] which is valid throughout most of the stratosphere. Above 30 km, as the ozone density decreases the capability of the reaction NO + O$_3$ to convert NO to NO$_2$, reaction of NO$_2$ with O becomes increasingly important as atomic O abundance increases due to more efficient O$_3$ photolysis. Consequently, at increasing altitudes NO becomes the dominant form of the daytime nitrogen oxide family.

The extent to which the measurements of Fig. 4 can be compared is limited mainly by differences in ozone profiles at the time of the respective observations and also, to a lesser degree, by variations in JNO$_2$ and temperature. In particular, the balloon measurements of NO$_2$/NO by Ridley et al. [1987] at altitudes which overlap the ER-2 data were reported with ozone abundances higher by 10-50% and temperatures higher by 10K, thus accounting for the higher ratio observed.

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