

SIMULTANEOUS, IN SITU MEASUREMENTS OF OH, HO<sub>2</sub>, O<sub>3</sub>, AND H<sub>2</sub>O:  
 A TEST OF MODELED STRATOSPHERIC HO<sub>x</sub> CHEMISTRY

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**Abstract.** Simultaneous, in situ measurements of OH, HO<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub> from 37–23 km are reported. The partitioning between OH and HO<sub>2</sub> and the total HO<sub>x</sub> concentration are compared with expected steady-state values. The ratio of HO<sub>2</sub> to OH varies from less than 2 at 36 km to more than 3 at 25 km; in the lower stratosphere this ratio is nearly a factor of two less than predicted. The data are used to calculate HO<sub>x</sub> production and loss rates. The measured HO<sub>x</sub> mixing ratio is consistent with production dominated by the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O, and loss controlled by NO<sub>y</sub> below 28 km and HO<sub>x</sub> above 30 km. The steady-state concentration of H<sub>2</sub>O<sub>2</sub> is inferred from the measured HO<sub>2</sub> concentration and calculated photolysis rate. The maximum H<sub>2</sub>O<sub>2</sub> mixing ratio (at 33 km) is predicted to be less than 0.2 ppb.

## Introduction

The odd-hydrogen family (H+OH+HO<sub>2</sub>) plays a crucial role in determining the concentration of stratospheric ozone. Although catalytic cycles of HO<sub>x</sub> result in significant odd oxygen loss, especially in the upper (> 40 km) and lower (< 20 km) stratosphere, it is primarily the complex interactions of the HO<sub>x</sub> family with the NO<sub>x</sub> and ClO<sub>x</sub> families that make an understanding of this chemistry important. In particular, there is a pressing need to predict the response of stratospheric ozone to the increasing burden of chlorine. Except in the perturbed polar regions, the rate of return of HCl, an inert reservoir species, to ClO<sub>x</sub> is determined solely by the OH density. In this paper, we use the results of a balloon-borne experiment launched from Palestine, Texas, on August 25, 1989, to address the fundamental question of what controls the stratospheric OH density.

## Experimental / Calculation

The instruments employed on the gondola are described elsewhere. Briefly, the measurements are made as the payload descends at approximately 5 m s<sup>-1</sup> from a float altitude of 37 km. The OH concentration is determined by laser-induced fluorescence (LIF) [Stimpfle et al., 1990]. HO<sub>2</sub> is converted to OH by addition of NO to the contained flow upstream of the LIF OH axis [Stimpfle et al., 1990]. O<sub>3</sub> is determined by UV photometry [Weinstock et al., 1986]. H<sub>2</sub>O is measured by Lyman- $\alpha$  photofragment fluorescence [Weinstock et al., 1990]. Pressure is mea-

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sured by MKS pressure transducers. The temperature is recorded by calibrated thermistors which are located outside the gondola boundary layer.

The observed profiles of O<sub>3</sub>, OH, HO<sub>2</sub>, H<sub>2</sub>O, pressure, and temperature are shown in Figure 1. The controlled descent at 32.2°N, 99.6°W began at 2202 and ended at 2248 UT (1623–1709 CDT). The solar zenith angle (SZA) varied from 51° to 61° during the descent.

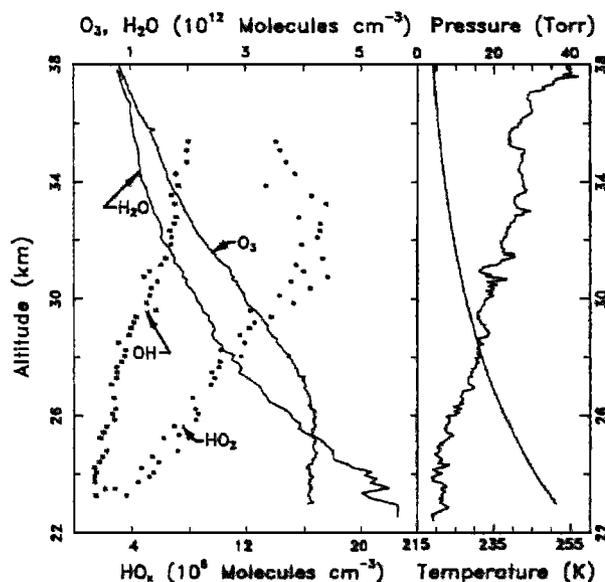


Fig. 1. Results from the balloon-borne in situ experiment flown on August 25, 1989. Measured profiles of OH, HO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, pressure and temperature are shown. The solar zenith angle varied from 51° at 37 km to 61° at 23 km.

The radiation field is calculated by a modified plane-parallel model developed at the Naval Research Laboratory [Anderson, 1983]. *J*-values are calculated for the appropriate SZA using absorption cross-sections from the JPL evaluation [1988] and the observed ozone, pressure, and temperature profiles.

Unless otherwise noted, the concentrations of unmeasured species are based on the mid-latitude profiles from WMO [1986]. As suggested by Weinheimer and Ridley [1990], the NO mixing ratio determined by balloon-borne instruments above 30 km is reduced and brought into coincidence with the data taken from rockets by Horvath [1983]. The O(<sup>1</sup>D) concentration is calculated from *J*<sub>O<sub>3</sub></sub>, the measured ozone mixing ratio, and O(<sup>1</sup>D) quenching rate constants. The concentration of pernitric acid (lifetime ≤ 1 day) is calculated by assuming photochemical steady state:

$$[\text{HOONO}_2] \approx \frac{k_{(\text{HO}_2 + \text{NO}_2 + \text{M})}[\text{M}][\text{NO}_2][\text{HO}_2]}{J_{\text{HOONO}_2} + k_3[\text{OH}]}$$

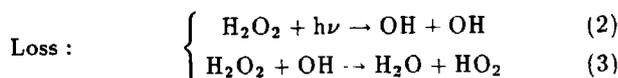
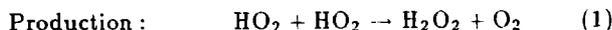
In this analysis, all rate constants are taken, with their respective uncertainties, from the JPL Panel recommendation [1988]. The error analysis represents a  $1\sigma$  distribution in which the uncertainty in the rate constants was assumed to be log-normally distributed, with the recommended value being the most probable. The uncertainties in the concentrations of unmeasured species, listed in Table 1, are assumed to be normally distributed. The final uncertainties in the calculations below are determined by Monte Carlo error analysis.

### Discussion

Simultaneous, in situ measurements allow quantitative tests of simple photochemical steady-state relationships. For species with short lifetimes, such as OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>, the proposed mechanisms controlling production, loss and partitioning in a key free-radical system can be tested.

#### The Steady-State Concentration of H<sub>2</sub>O<sub>2</sub>

The only known source of stratospheric hydrogen peroxide is the self reaction of HO<sub>2</sub>. The principal losses of peroxide are photolysis and reaction with OH. From the measurements of HO<sub>2</sub> and OH and the calculated radiation field, the photochemical steady-state concentration of H<sub>2</sub>O<sub>2</sub> can be determined:



and so:

$$[\text{H}_2\text{O}_2] = \frac{k_1[\text{HO}_2][\text{HO}_2]}{J_2 + k_3[\text{OH}]} \quad (4)$$

Figure 2 shows the calculated steady-state concentration of H<sub>2</sub>O<sub>2</sub> predicted from the measured concentration of HO<sub>2</sub> and OH. Also shown in Figure 2 are the measurements of Chance and Traub [1987], and Waters et al. [1981] (both reported as tentative), as well as the upper limits determined by May and Webster [1989], de Zafra et al. [1985], and Larsen et al. [1985].

The inferred value of the hydrogen peroxide mixing ratio is an order of magnitude lower than the measurement of Chance and Traub at 37 km and Waters at 31 km.

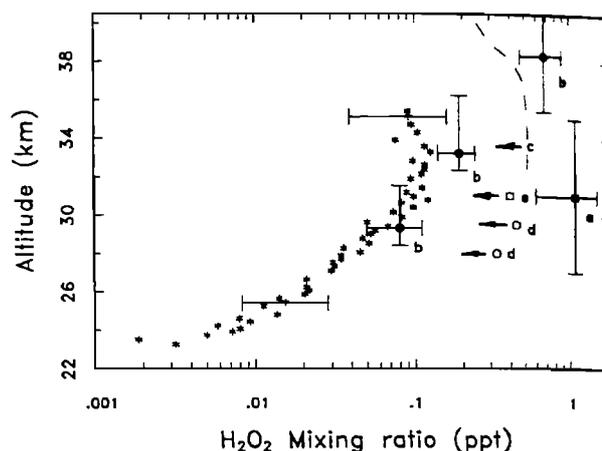
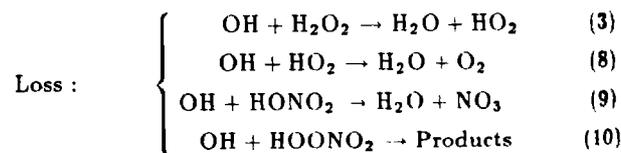
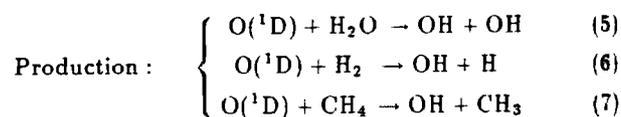


Fig. 2. Calculated steady state hydrogen peroxide concentration (\*). Also shown are the measurements of (a) Waters et al. [1981], (b) Chance and Traub [1987], and the upper limit measurements of (c) de Zafra et al. [1985], (d) Larsen et al. [1985], and (e) May and Webster [1989].

Chance and Traub now feel that their earlier measurement is in error and that the peak concentration is below 100 ppt (K. Chance; personal communication). It seems likely that the measurement by Waters is also in error.

#### HO<sub>x</sub>: Production and Loss

In the upper and middle stratosphere, the sum of the concentrations of OH and HO<sub>2</sub> is thought to be controlled by only a few reactions.



Shown in Figure 3 are the calculated production and loss rates between 23–37 km. Reaction (5) is the dominant production term, constituting greater than 90% of the total. The calculated loss rates are shown explicitly. Based on the calculated H<sub>2</sub>O<sub>2</sub> concentration, reaction (3)

TABLE 1. Concentrations used in the modeling of HO<sub>x</sub> chemistry.

Altitude (km)	[M] (10 <sup>17</sup> cm <sup>-3</sup> )	[NO] (10 <sup>9</sup> cm <sup>-3</sup> )	[NO <sub>2</sub> ] (10 <sup>9</sup> cm <sup>-3</sup> )	[HNO <sub>3</sub> ] (10 <sup>8</sup> cm <sup>-3</sup> )	[HNO <sub>4</sub> ] (10 <sup>7</sup> cm <sup>-3</sup> )	[O( <sup>3</sup> P)] (10 <sup>7</sup> cm <sup>-3</sup> )	[O( <sup>1</sup> D)] (cm <sup>-3</sup> )
36	1.6	1.3 ± 0.6	1.1 ± 0.4	1.4 ± 0.6	0.8 ± 0.6	29.0 ± 8.7	93 ± 45
34	2.2	1.4 ± 0.7	1.4 ± 0.6	4.2 ± 1.7	1.2 ± 0.9	18.0 ± 5.4	67 ± 33
32	2.9	1.5 ± 0.8	1.7 ± 0.7	8.7 ± 3.5	3.3 ± 2.5	10.5 ± 3.1	40 ± 20
28	5.4	1.3 ± 0.5	1.6 ± 0.7	26.4 ± 10.6	7.8 ± 5.8	3.2 ± 0.9	13 ± 7
26	7.4	1.2 ± 0.4	1.4 ± 0.6	44.6 ± 17.8	9.1 ± 6.8	1.8 ± 0.5	7 ± 3
24	10.0	1.1 ± 0.4	1.2 ± 0.5	69.1 ± 27.6	8.8 ± 6.6	0.9 ± 0.3	4 ± 2

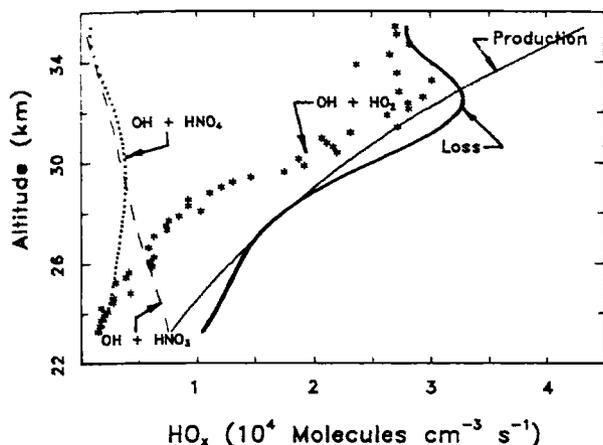


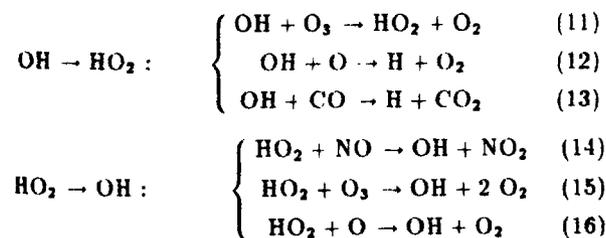
Fig. 3. Calculated odd-hydrogen production and loss rates. The production is primarily from the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O. The individual and total loss rates are shown explicitly: (\*) =  $k_8[\text{OH}][\text{HO}_2]$ ; (dashed) =  $k_9[\text{OH}][\text{HNO}_3]$ ; (dotted) =  $k_{10}[\text{OH}][\text{HNO}_4]$ . Uncertainty in the total loss and production rates is approximately  $\pm 60\%$ .

does not constitute an important loss of HO<sub>x</sub>. Above 28 km, reaction (8) is the primary odd-hydrogen loss process. In the lower stratosphere, the loss becomes dominated by the NO<sub>x</sub> reactions (9) and (10). Because neither nitric nor pernitric acid were measured, there is large uncertainty in the net rates of these reactions.

The calculated loss and production rates of HO<sub>x</sub> are in rough agreement throughout the altitude range. Above 33 km HO<sub>x</sub> loss falls below the calculated production rate, with a disparity of approximately 35% at the highest altitude. Given the large uncertainty in both the HO<sub>x</sub> production and loss rates ( $\approx 60\%$ ), and the paucity of data above 33 km it is not clear what, if any, significance to apply to this result. In particular, because of the quadratic dependence of reaction (8) on [HO<sub>x</sub>], any error in the measured OH density is magnified in calculating the absolute rate of reaction (8).

#### The Partitioning between HO<sub>2</sub> and OH

Throughout the stratosphere, the ratio of HO<sub>2</sub> to OH is thought to be controlled by six reactions:



The first-order rates for these processes are shown in Figure 4. The H atoms produced in reactions (12) and (13) are converted almost exclusively to HO<sub>2</sub> by reaction with O<sub>2</sub>. The rates of reactions (12) and (13) are not shown because reaction (11) dominates the conversion of OH to HO<sub>2</sub>. Additional pathways exist for HO<sub>2</sub> conversion to OH through reactions with ClO, HO<sub>2</sub>, and

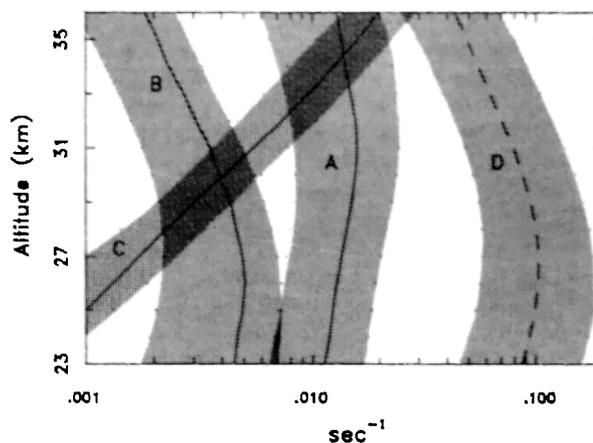


Fig. 4. First-order rates for the cycling of HO<sub>2</sub> to OH (solid): A =  $k_{14}[\text{NO}]$ ; B =  $k_{15}[\text{O}_3]$ ; C =  $k_{16}[\text{O}]$ , and for OH to HO<sub>2</sub> (dashed): D =  $k_{11}[\text{O}_3]$ . Shaded areas represent a  $1\sigma$  estimate of the uncertainty.

the three-body reaction with NO<sub>2</sub>. Photolysis of the products, HOCl, H<sub>2</sub>O<sub>2</sub>, and HNO<sub>4</sub>, generates OH but does not add more than 10% to the total first-order rate for the cycling of HO<sub>2</sub> to OH. The calculated steady-state and measured ratios of [HO<sub>2</sub>] to [OH] are shown in Figure 5. Although the measured and calculated ratios agree within their respective uncertainties, the divergence is marked in the lower stratosphere, especially considering the excellent agreement at the highest altitudes. The measured ratio of HO<sub>2</sub> to OH is a factor of two lower than expected at 25 km. Three possible explanations for this result are: (1) error in the first-order rates; or (2) error in the measured ratio; or (3) incompletely described chemistry.

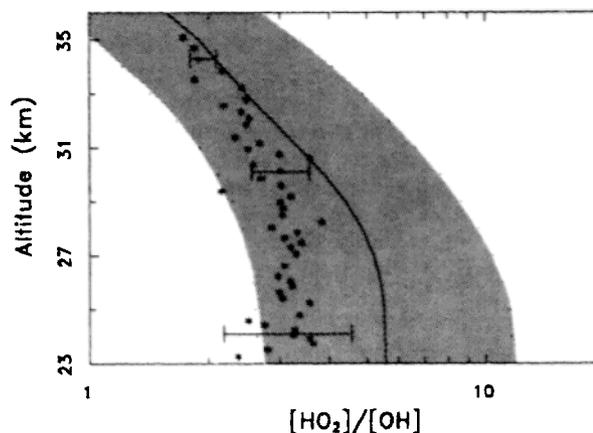


Fig. 5. Calculated (solid) and measured (\*) ratio of [HO<sub>2</sub>] to [OH]. Shaded area represents a  $1\sigma$  estimate of the uncertainty in the calculated ratio.

Despite a decade of improvement in the kinetics data base, the largest source of uncertainty in the calculated ratio is the uncertainty in the rate constants at low temperatures. Below 28 km the ratio is expected to be controlled by reactions (11), (14), and (15). Further laboratory studies of these reactions are clearly needed. Uncertainty

is also introduced by the lack of simultaneous NO measurements. To fully explain the difference between the calculated and measured ratios, the NO density would have to be 250% higher than the value used here—a concentration larger than any previously measured.

Because HO<sub>2</sub> is measured by conversion to OH, many sources of error in the measurement of the concentration of OH and HO<sub>2</sub> cancel when calculating the ratio. In particular, the measured ratio is insensitive to the calibration of the instrument for OH or the assumed OH fluorescence efficiency. The major remaining sources of uncertainty are the conversion efficiency of HO<sub>2</sub> to OH and, to a smaller extent, the precision of the data. The latter is shown explicitly in Figure 5. As discussed elsewhere [Stimpfle et al., 1990], the conversion of HO<sub>2</sub> to OH with NO addition is complicated by secondary chemistry. As NO is added to the flow, OH is lost in a three-body reaction with NO. The error bars in Figure 5 represent the estimated uncertainty in the conversion process as derived from the accepted values and uncertainties of the bimolecular and termolecular reactions.

The most intriguing explanation of the difference between the measured and calculated ratios is missing chemistry. To explain the measured ratio, a reaction converting HO<sub>2</sub> to OH with an altitude-dependent rate is required. The first-order rate of this reaction would have to be approximately 0.02 s<sup>-1</sup> at 25 km. This in turn requires that the excess reagent be present at concentrations above 2 ppbv, assuming an upper limit of 10<sup>-10</sup> cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> for the second-order rate constant. Resolution of the issue of missing chemistry clearly requires a reduction of the uncertainties discussed above.

### Conclusions

The power of simultaneous, in situ measurements of a large suite of compounds is unrivaled in its ability to investigate the mechanisms controlling stratospheric ozone chemistry. From this experiment, a picture of the HO<sub>x</sub> chemistry emerges that involves a transition from a self-buffered system in the upper stratosphere to one dominated by nitrogen chemistry below 30 km. It is this latter regime that is most poorly understood, and probably most subject to perturbations from changes in the composition of the stratosphere.

Further experiments are clearly needed before we can accurately predict the response of HO<sub>x</sub>, and thus odd oxygen, to such changes as the increasing concentrations of N<sub>2</sub>O, CH<sub>4</sub>, and the CFCs. Uncertainty in the measured rates of many important reactions are too large to fully test the consistency of the proposed mechanisms. This analysis would be greatly enhanced by the additional, simultaneous measurements of O, NO, NO<sub>2</sub>, and HNO<sub>3</sub>.

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