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EFFECT OF ODD HYDROGEN ON OZONE DEPLETION BY CHLORINE REACTIONS

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Abstract. The odd hydrogen species, especially OH and HO₂ are important in the chemistry of the natural stratosphere because of their direct reactions with O and O₃ and their role in nitrogen oxide (NO_x) cycles. When chlorine is added to the stratosphere the interaction of NO_x, HO_x and ClX species yields several potential feedback effects for O₃ perturbations, some stabilizing and some destabilizing. Here we focus on the effects of HO_x on O₃ changes due to ClX injections. As ClX selectively attacks the ozone layer above 28 km the layer below tends to be thickened by the increased incidence of solar UV. If HO_x densities are high they dampen this radiative feedback and prevent the healing at low altitudes. We demonstrate how the ozone-layer shape changes under the influence of injected ClX for several choices of key HO_x reaction rates. These same reaction rates exert partial control over the apportioning of Cl atoms among HCl, ClO and Cl, over the total amount of HO_x, the ratios of OH to HO₂ and H₂O₂ and the ratio of [NO + NO₂] to [HNO₃]. The uncertainty in these rates leads to at least a factor of three uncertainty in predicted ozone reductions due to ClX injections.

This paper emphasizes the important role odd hydrogen species (H, OH, HO₂, H₂O₂) can play in stratospheric chemistry when ClX, or odd chlorine (HCl, ClO, Cl) is present. Earlier we proposed that a de-stabilizing feedback on stratospheric O₃ is possible, particularly if O₃ concentrations below 25 km can increase as O₃ concentrations above that altitude decrease [Liu et al., 1976a]. Here we discuss how two chemical reaction rates determine HO_x's role in a chlorine-polluted stratosphere and we show ozone-layer behavior for a range of values of each. The total ozone column and the layer shape are sensitive to these rates as is the apportioning of Cl atoms among HCl, ClO, and Cl. We draw attention to the role HO₂ and OH play in the presence of ClX. In the upper stratosphere they serve as chlorine chain terminators and regenerators. In the lower stratosphere they tend to neutralize the effectiveness of a radiative feedback mechanism that causes increases in ozone density at low altitudes to accompany decreases at high altitudes.

Two HO_x reactions are keys to these effects and their rate constants are not well known:

and

(R1) determines the rate at which chemically active odd hydrogen is converted to much less active H₂O. (R2) is important in exerting control over the ratio of OH and HO₂ concentrations. Together (R1) and (R2) influence the amount of HO_x in equilibrium with stratospheric H₂O, CH₄ and H₂. In turn, OH and HO₂ densities regulate the amount that the stratospheric ozone column can be reduced by injections of odd chlorine. Above 30 km the Cl-ClO catalytic cycle in ozone removal is important when Cl is produced from chlorofluorocarbon photolysis. The cycle consists of the chain

This ozone-destroying chain is interrupted mainly by

OH affects the efficiency of ozone destruction by ClX in this region. It is the principal species that re-initiates the chain reactions, liberating Cl atoms from HCl through

[Stolarski and Cicerone, 1974]. Depending on rate constants for (R1) and (R2), reaction (R6) can dominate (R5) as a chain terminator, at least for altitudes above 30 km. Thus, one has OH acting to enhance ClX removal of O₃ through (R7) while HO₂ impedes it through (R6). Generally the lower the rate constant, k₁, for (R1) and the higher the rate constant, k₂, for (R2) the greater the amount of OH (and HO_x) there will be for given amounts of H₂O and CH₄. The more OH, the more ClO there will be for a given ClX concentration, and thus the more effective a given ClX concentration will be against O₃. Most models have used either large values for k₁ (2 × 10⁻¹⁰ cm³sec⁻¹) or relatively small values for k₂ (8 × 10⁻¹¹ exp[-500/T]), or both. Yet the evidence for these choices is tenuous. In the remainder of this paper we refer to the above value for k₁ as "high k₁" and the above value for k₂ as "low k₂". This value of k₁ [Hochanadel et al., 1972] seems to be very high [Kaufman, 1975]. The k₂ value above was estimated by Lloyd [1974]. Furthermore, we note below that this combination of k₁ and k₂ is difficult to reconcile with the only measurements of OH densities in the upper atmosphere to date.

Below the ozone peak, odd hydrogen controls the effectiveness of ClX in reducing the total ozone column in a different way. ClX selectively attacks the upper part of the ozone layer [see e.g., Wofsy and McElroy, 1974; Cicerone et al., 1974; or Rowland and Molina, 1975] thereby reducing its opacity to solar radiation short of 3100Å. The increase in flux below 2440Å can create more O₃ in the lower part of the layer. In this way the concentration of O₃ below say, 25 km tends to increase as the amount of O₃ diminishes at higher altitudes. This "healing" effect tempers the overall destructiveness of a specified amount of ClX. However, the growth in O₃ density below the peak tends to be counteracted by enhanced production of HO_x there from H₂O and CH₄ interacting with O(¹D). As the O₃ density grows so does the creation rate of O(¹D) from ozone photolysis, and so does the conversion of H₂O and CH₄ to HO_x (and N₂O to NO_x). If k_1 is large the density of HO_x in a steady state with H₂O is small and the healing effect of O₃ production from increased UV below the peak tends to be significant. However, if k_1 is small enough, the growth in odd hydrogen density will be so large as ClX increases that it partially compensates by catalytic destruction of O₃ for the enhanced production of O₃ below 25 km. Thus, a low k_1 increases the destructiveness of a given amount of ClX for O₃ for two reasons, one operating above 25 km, the other below. This will be especially so if k_2 is high (and the HO_x is mostly in the form of OH near 40 km). If, for example k_1 were $2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (low k_1) and k_2 were $4 \times 10^{-10} \exp(-500/T) (5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1})$ near 40 km (high k_2), 1 ppb of ClX would reduce the amount of ozone in the atmosphere by 2.2%, and 5 ppb ClX by 11%. With high k_1 and low k_2 , the values assumed in many models, we would predict only a 0.7% ozone reduction for 1 ppb ClX and 4.3% for 5 ppb ClX. We calculated these ozone reductions with the Liu et al. [1976a] model using Hunten's eddy mixing rates, $k_3 = 4.3 \times 10^{-11} \exp(-350/T)$ [Anderson et al., 1975], $k_5 = 7.44 \times 10^{-12} \exp(-1226/T)$ [Davis et

Figure 1: Calculated ozone profiles for a chlorine-free stratosphere and in steady state with a 5 ppb mixing ratio of odd chlorine. Also shown is the total rate of destruction of O₃ by OH and HO₂ below 36 km, calculated with "high" k_1 and "high" k_2 . Note the increased O₃ concentration below 28 km and the decrease in O₃ above 28 km.

Figure 2: Same as Figure 1 only with "low" k_1 and "low" k_2 (these rate constants are defined in the text). The rates at which odd hydrogen destroys ozone are shown for no chlorine, 1 ppb, and 5 ppb. Note that the O₃ concentration is decreased everywhere above 22 km by ClX and there is no appreciable ozone healing in the lower stratosphere.

al., 1975], $k_6 = 2 \times 10^{-11}$ and with the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ included. Calculations were performed assuming a steady state for various concentrations of odd chlorine. The ClX density profile is that appropriate for chlorofluorocarbon photolysis [see for example, Cicerone et al., 1974], i.e., the mixing ratio of ClX reaches an asymptotic value above 35 km.

To illustrate the odd hydrogen effects mentioned above we show ozone distributions for no ClX and for 5 ppb ClX (the high altitude asymptotic mixing ratio) calculated for two cases: (1) high k_1 , high k_2 , (2) low k_1 , low k_2 . We show Case 1 results in Figure 1 and Case 2 in Figure 2, along with curves showing the sum of the rates of destruction of O₃ by the reactions

and

For case 1 the ozone density at every altitude up to 28 km increases as ClX grows from 0 to 5 ppb because of the enhanced production of O₃ there resulting from the reduction of O₃ opacity above 30 km as a result of the ClX chain reaction. On the other hand for Case 2 (k_1 small) the ozone profile is virtually unaffected below 22 km as the ClX concentration increases from 0 to 5 ppb. The top of the layer gets eaten away by the Cl-ClO catalytic chain whose efficiency is enhanced compared to case 1 by the faster conversion of HCl to Cl by OH, although not as much as if k_2 were larger. In addition, the enhanced production of O₃ below 28 km resulting from the increase in UV transmission is compensated in this case by enhanced destruction by HO_x. The HO_x density, in balance with the H₂O destruction by O(¹D) and CH₄ oxidation, is much larger than in Case 1 owing to the low rate constant for k_1 . Note the large increase in the

Table 1: Calculated diurnally averaged concentrations of OH and HO₂ at 40 km for four combinations of the two rate constants k₁ and k₂. Also shown are the corresponding predicted ozone column reductions in steady state with 1 ppb and 5 ppb added odd chlorine.

	k ₁	k ₂	[OH] ₄₀	[HO ₂] ₄₀	Column O ₃ reduction (%)	
			(10 ⁷ cm ⁻³)		1 ppb ClX	5 ppb ClX
a.	High	Low	0.43	1.6	0.59	3.6
b.	High	High	1.0	0.8	0.72	4.3
c.	Low	Low	1.38	5.2	1.7	9.1
d.	Low	High	3.34	2.6	2.2	11.0

rate of destruction of O₃ by HO_x below 25 km as ClX increases in Figure 2 compared to Figure 1. Destruction of O₃ above 30 km is not compensated by recovery below that altitude, hence the increased effectiveness of ClX in destroying ozone when k₁ is small.

Other mechanisms, in principle, might also be important in enhancing the ClX destruction of ozone in the presence of large HO_x concentrations. We have conducted a search for the dominant process and found it to be the one we have discussed here. For example, the erosion of the topside of the ozone layer enhances the rate of production of NO_x from N₂O on the bottomside because of the increase in the rate of generation of O(¹D). However, the altitude of maximum production of NO_x moves downward as the amount of ClX increases, thus impeding NO_x buildup. Hence, the increase in NO_x density is small in the region below the ozone peak and there is little difference in the NO_x density between case 1 and case 2.

Some results at higher altitudes are illustrated in Table 1. For four combinations of k₁ and k₂, diurnally averaged OH and HO₂ densities at 40 km are presented along with the reduction in total ozone by 1 ppb added ClX and 5 ppb added ClX. One sees that the total amount of HO_x, the ratio of OH and HO₂ densities, and the calculated ozone reduction due to added ClX all are sensitive to the rates k₁ and k₂.

Recent measurements by J. G. Anderson [1975] show an OH density of $2 \pm 1.5 \times 10^7 \text{cm}^{-3}$ at 40 km, in late afternoon (solar zenith angle = 80°). This result cannot definitely exclude any combination of k₁ and k₂ considered here, although the central value suggests that k₁ should be low. A complete time-dependent diurnal calculation with an extended version of our model [Liu et al., 1976b] predicts for the 4 cases as 80° zenith angle:

	k ₁	k ₂	OH at 40 km (10 ⁷ cm ⁻³)
a.	High	Low	0.41
b.	High	High	0.75
c.	Low	Low	1.40
d.	Low	High	3.00

Earlier rocket measurements of OH [Anderson, 1971] between 45 km and 70 km are marginally

consistent with k₁ low and k₂ high, and with k₁ high and k₂ low. The model for the latter case (a) barely scrapes the lower border of the error bars for the measurement; for the former (case d) the model values are above his limits at low altitudes. k₁ and k₂ both low or both high fit the measurements very well.

Finally, the rates k₁, k₂ and that for (R6) have a very large effect on the calculated Cl, ClO, and HCl density distributions. The Cl density near 45 km expected for 1 ppb ClX can be as small as $8 \times 10^4 \text{cm}^{-3}$ with a combination of k₁ high, k₂ low and k₆ large; ($10^{-10} \text{cm}^3 \text{sec}^{-1}$) or as large as 10^6cm^{-3} for a combination of k₁ small, k₂ large and k₆ small ($2 \times 10^{-11} \text{cm}^3 \text{sec}^{-1}$). Figure 3 illustrates the range of Cl, ClO and HCl concentrations (at 1 ppb ClX) found for k₆ = 2×10^{-11} and the four combinations of k₁ and k₂. Lower values for k₆ yield less HCl and more Cl and ClO everywhere; higher k₆ results in more HCl and less Cl and ClO everywhere.

To conclude, it is clear that the significance of several possible feedback effects involving HO_x in a chlorine-polluted stratosphere must be determined. Measurements of the rates k₁, k₂ and k₆ are needed at relevant temperatures as

Figure 3: Calculated Cl, ClO and HCl concentrations vs. altitude when their total (ClX) mixing ratio is 1 ppb above 35 km, for four combinations of k₁ and k₂: (• — • for high k₁, low k₂), (— — — for high k₁, high k₂), (— — — for low k₁, low k₂), (.... for low k₁, high k₂). k₆ is 2×10^{-11} (see text).

are atmospheric measurements of OH and HO₂. Such laboratory and atmospheric data on OH and HO₂ are also needed to plan and interpret measurements of odd chlorine species as our Figure 3 shows. Until such studies are completed the amount of ozone reduction by a given mixing ratio of ClX will remain very uncertain. Reduction as large as those predicted before the re-evaluation of k_3 and k_5 [Crutzen, 1974; Cicerone et al., 1974; Wofsy et al., 1975] cannot be excluded yet.

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