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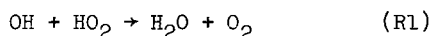
## EFFECT OF ODD HYDROGEN ON OZONE DEPLETION BY CHLORINE REACTIONS

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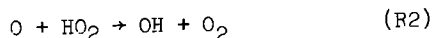
**Abstract.** The odd hydrogen species, especially OH and HO<sub>2</sub> are important in the chemistry of the natural stratosphere because of their direct reactions with O and O<sub>3</sub> and their role in nitrogen oxide (NO<sub>x</sub>) cycles. When chlorine is added to the stratosphere the interaction of NO<sub>x</sub>, HO<sub>x</sub> and ClX species yields several potential feedback effects for O<sub>3</sub> perturbations, some stabilizing and some destabilizing. Here we focus on the effects of HO<sub>x</sub> on O<sub>3</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub>, the ratios of OH to HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> and the ratio of [NO + NO<sub>2</sub>] to [HNO<sub>3</sub>]. 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, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) 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 O<sub>3</sub> is possible, particularly if O<sub>3</sub> concentrations below 25 km can increase as O<sub>3</sub> concentrations above that altitude decrease [Liu et al., 1976a]. Here we discuss how two chemical reaction rates determine HO<sub>x</sub>'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 HO<sub>2</sub> 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.

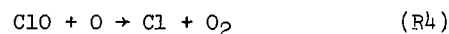
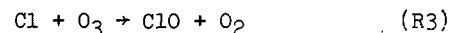
Two HO<sub>x</sub> reactions are keys to these effects and their rate constants are not well known:



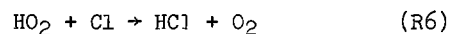
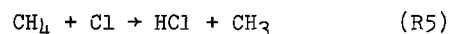
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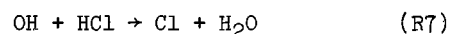
(R1) determines the rate at which chemically active odd hydrogen is converted to much less active H<sub>2</sub>O. (R2) is important in exerting control over the ratio of OH and HO<sub>2</sub> concentrations. Together (R1) and (R2) influence the amount of HO<sub>x</sub> in equilibrium with stratospheric H<sub>2</sub>O, CH<sub>4</sub> and H<sub>2</sub>. In turn, OH and HO<sub>2</sub> 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 O<sub>3</sub> through (R7) while HO<sub>2</sub> impedes it through (R6). Generally the lower the rate constant, k<sub>1</sub>, for (R1) and the higher the rate constant, k<sub>2</sub>, for (R2) the greater the amount of OH (and HO<sub>x</sub>) there will be for given amounts of H<sub>2</sub>O and CH<sub>4</sub>. 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 O<sub>3</sub>. Most models have used either large values for k<sub>1</sub> (2 x 10<sup>-10</sup> cm<sup>3</sup>sec<sup>-1</sup>) or relatively small values for k<sub>2</sub> (8 x 10<sup>-11</sup> 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 k<sub>1</sub> as "high k<sub>1</sub>" and the above value for k<sub>2</sub> as "low k<sub>2</sub>". This value of k<sub>1</sub> [Hochanadel et al., 1972] seems to be very high [Kaufman, 1975]. The k<sub>2</sub> value above was estimated by Lloyd [1974]. Furthermore, we note below that this combination of k<sub>1</sub> and k<sub>2</sub> 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 O<sub>3</sub> in the lower part of the layer. In this way the concentration of O<sub>3</sub> below say, 25 km tends to increase as the amount of O<sub>3</sub> diminishes at higher altitudes. This "healing" effect tempers the overall destructiveness of a specified amount of ClX. However, the growth in O<sub>3</sub> density below the peak tends to be counteracted by enhanced production of HO<sub>x</sub> there from H<sub>2</sub>O and CH<sub>4</sub> interacting with O(<sup>1</sup>D). As the O<sub>3</sub> density grows so does the creation rate of O(<sup>1</sup>D) from ozone photolysis, and so does the conversion of H<sub>2</sub>O and CH<sub>4</sub> to HO<sub>x</sub> (and N<sub>2</sub>O to NO<sub>x</sub>). If k<sub>1</sub> is large the density of HO<sub>x</sub> in a steady state with H<sub>2</sub>O is small and the healing effect of O<sub>3</sub> production from increased UV below the peak tends to be significant. However, if k<sub>1</sub> is small enough, the growth in odd hydrogen density will be so large as ClX increases that it partially compensates by catalytic destruction of O<sub>3</sub> for the enhanced production of O<sub>3</sub> below 25 km. Thus, a low k<sub>1</sub> increases the destructiveness of a given amount of ClX for O<sub>3</sub> for two reasons, one operating above 25 km, the other below. This will be especially so if k<sub>2</sub> is high (and the HO<sub>x</sub> is mostly in the form of OH near 40 km). If, for example k<sub>1</sub> were 2 x 10<sup>-11</sup> cm<sup>3</sup>sec<sup>-1</sup> (low k<sub>1</sub>) and k<sub>2</sub> were 4 x 10<sup>-10</sup> exp(-500/T) (5 x 10<sup>-11</sup> cm<sup>3</sup>sec<sup>-1</sup> near 40 km) (high k<sub>2</sub>), 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<sub>1</sub> and low k<sub>2</sub>, 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<sub>3</sub> = 4.3 x 10<sup>-11</sup> exp[-350/T] [Anderson et al., 1975], k<sub>5</sub> = 7.44 x 10<sup>-12</sup> exp[-1226/T] [Davis et

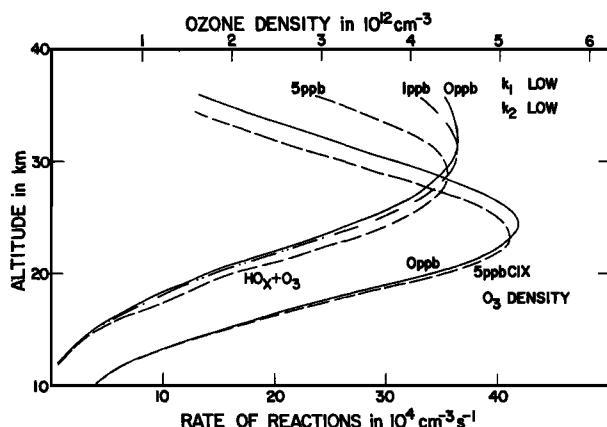


Figure 1: Calculated ozone profiles for a chlorine-free stratosphere and in steady state with a 5 ppb mixing ratio of odd chlorine. Also shown is the total rate of destruction of O<sub>3</sub> by OH and HO<sub>2</sub> below 36 km, calculated with "high" k<sub>1</sub> and "high" k<sub>2</sub>. Note the increased O<sub>3</sub> concentration below 28 km and the decrease in O<sub>3</sub> above 28 km.

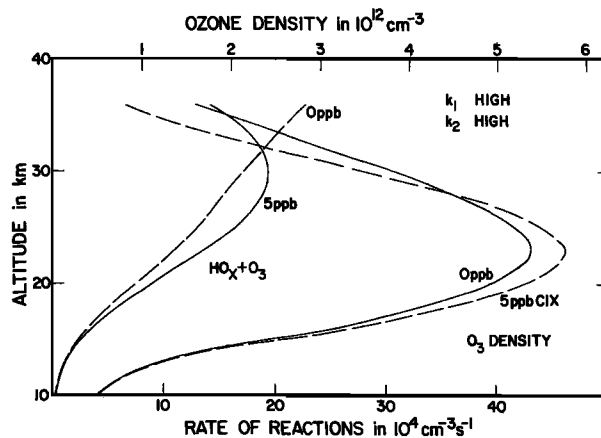
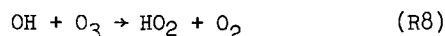


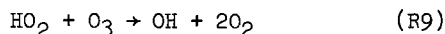
Figure 2: Same as Figure 1 only with "low" k<sub>1</sub> and "low" k<sub>2</sub> (these rate constants are defined in the text). The rates at which odd hydrogen destroys ozone are shown for no chlorine, 1 ppb, and 5 ppb. Note that the O<sub>3</sub> concentration is decreased everywhere above 22 km by ClX and there is no appreciable ozone healing in the lower stratosphere.

al., 1975], k<sub>6</sub> = 2 x 10<sup>-11</sup> and with the reaction CO + OH → CO<sub>2</sub> + 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<sub>1</sub>, high k<sub>2</sub>, (2) low k<sub>1</sub>, low k<sub>2</sub>. 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 O<sub>3</sub> 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 O<sub>3</sub> there resulting from the reduction of O<sub>3</sub> opacity above 30 km as a result of the ClX chain reaction. On the other hand for Case 2 (k<sub>1</sub> 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<sub>2</sub> were larger. In addition, the enhanced production of O<sub>3</sub> below 28 km resulting from the increase in UV transmission is compensated in this case by enhanced destruction by HO<sub>x</sub>. The HO<sub>x</sub> density, in balance with the H<sub>2</sub>O destruction by O(<sup>1</sup>D) and CH<sub>4</sub> oxidation, is much larger than in Case 1 owing to the low rate constant for k<sub>1</sub>. Note the large increase in the

Table 1: Calculated diurnally averaged concentrations of OH and HO<sub>2</sub> at 40 km for four combinations of the two rate constants k<sub>1</sub> and k<sub>2</sub>. Also shown are the corresponding predicted ozone column reductions in steady state with 1 ppb and 5 ppb added odd chlorine.

	k <sub>1</sub>	k <sub>2</sub>	[OH] <sub>40</sub> (10 <sup>7</sup> cm <sup>-3</sup> )	[HO <sub>2</sub> ] <sub>40</sub> (10 <sup>7</sup> cm <sup>-3</sup> )	Column O <sub>3</sub> reduction (%)	
					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 O<sub>3</sub> by HO<sub>x</sub> below 25 km as ClX increases in Figure 2 compared to Figure 1. Destruction of O<sub>3</sub> above 30 km is not compensated by recovery below that altitude, hence the increased effectiveness of ClX in destroying ozone when k<sub>1</sub> is small.

Other mechanisms, in principle, might also be important in enhancing the ClX destruction of ozone in the presence of large HO<sub>x</sub> 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<sub>x</sub> from N<sub>2</sub>O on the bottomside because of the increase in the rate of generation of O(<sup>1</sup>D). However, the altitude of maximum production of NO<sub>x</sub> moves downward as the amount of ClX increases, thus impeding NO<sub>x</sub> buildup. Hence, the increase in NO<sub>x</sub> density is small in the region below the ozone peak and there is little difference in the NO<sub>x</sub> density between case 1 and case 2.

Some results at higher altitudes are illustrated in Table 1. For four combinations of k<sub>1</sub> and k<sub>2</sub>, diurnally averaged OH and HO<sub>2</sub> 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<sub>x</sub>, the ratio of OH and HO<sub>2</sub> densities, and the calculated ozone reduction due to added ClX all are sensitive to the rates k<sub>1</sub> and k<sub>2</sub>.

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 k<sub>1</sub> and k<sub>2</sub> considered here, although the central value suggests that k<sub>1</sub> 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 <sub>1</sub>	k <sub>2</sub>	OH at 40 km (10 <sup>7</sup> cm <sup>-3</sup> )
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 k<sub>1</sub> low and k<sub>2</sub> high, and with k<sub>1</sub> high and k<sub>2</sub> 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. k<sub>1</sub> and k<sub>2</sub> both low or both high fit the measurements very well.

Finally, the rates k<sub>1</sub>, k<sub>2</sub> 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 k<sub>1</sub> high, k<sub>2</sub> low and k<sub>6</sub> large; ( $10^{-10} \text{cm}^3 \text{sec}^{-1}$ ) or as large as  $10^6 \text{cm}^{-3}$  for a combination of k<sub>1</sub> small, k<sub>2</sub> large and k<sub>6</sub> 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 k<sub>6</sub> =  $2 \times 10^{-11}$  and the four combinations of k<sub>1</sub> and k<sub>2</sub>. Lower values for k<sub>6</sub> yield less HCl and more Cl and ClO everywhere; higher k<sub>6</sub> 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<sub>x</sub> in a chlorine-polluted stratosphere must be determined. Measurements of the rates k<sub>1</sub>, k<sub>2</sub> and k<sub>6</sub> are needed at relevant temperatures as

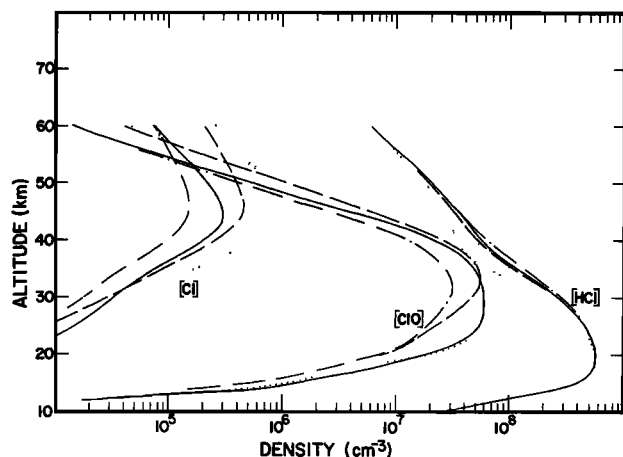


Figure 3: Calculated Cl, ClO and HCl concentrations vs. altitude when their total (ClX) mixing ratio is 1 ppb above 35 km, for four combinations of k<sub>1</sub> and k<sub>2</sub>: (· — · for high k<sub>1</sub>, low k<sub>2</sub>), (— — — for high k<sub>1</sub>, high k<sub>2</sub>), (— — — for low k<sub>1</sub>, low k<sub>2</sub>), (· · · · for low k<sub>1</sub>, high k<sub>2</sub>). k<sub>6</sub> is  $2 \times 10^{-11}$  (see text).

are atmospheric measurements of OH and HO<sub>2</sub>. Such laboratory and atmospheric data on OH and HO<sub>2</sub> 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<sub>3</sub> and k<sub>5</sub> [Crutzen, 1974; Cicerone et al., 1974; Wofsy et al., 1975] cannot be excluded yet.

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