THE CHEMISTRY OF ATMOSPHERIC BROMINE

Steven C. Wofsy, Michael B. McElroy and Yuk Ling Yung

Center for Earth and Planetary Physics
Harvard University, Cambridge, Massachusetts

Abstract. Bromine may act as a catalyst for recombination of ozone and could be more efficient than either nitric oxide or chlorine. The lower atmosphere contains small concentrations of gaseous bromine produced in part by marine activity, in part by volatilization of particulate material released during the combustion of leaded gasoline, with an additional contribution due to the use of methyl bromide as an agricultural fumigant. Observations by Lazrus et. al. (1975) indicate small concentrations of bromine, $\sim 10^{-11}$ (v/v), in the contemporary stratosphere and appear to imply a reduction of approximately 0.3% in the global budget of O_3. Estimates are given for future reductions in O_3 which might occur if the use of CH_3Br as an agricultural fumigant were to continue to grow at present rates.
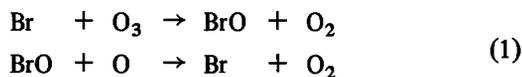
The chemistry of atmospheric ozone may be influenced to a remarkable extent by exceedingly small quantities of select stratospheric gases. Attention has focused in recent years on nitric oxide released by SST's (Johnston, 1971; Crutzen, 1972) and on chlorine produced by photodecomposition of chlorofluoromethanes (Molina and Rowland, 1974). This paper is devoted to a discussion of bromine. As we shall see, concentrations of bromine as small as 1 part in 10^{11} (v/v) can have an appreciable influence on ozone.

There are indications that the mixing ratio of gaseous forms of acidic bromine, represented most probably by HBr, according to the discussion below, may approach 10^{-11} in today's stratosphere (Lazrus et. al., 1975) with similar values observed in the troposphere (see below). The mixing ratio of acidic bromine appears to increase with increasing altitude between 15 and 19 km and there is evidence for similar behavior in the height distribution of particulate bromine (Lazrus et. al., 1975; Delany et. al., 1974). It is difficult to escape the conclusion that there must be a stratospheric source for particulate and gaseous acidic bromine.[†] Decomposition of methyl bromide offers a plausible explanation. Methyl bromide has been detected recently in surface waters of the ocean and in antarctic snow (R. Rasmussen, private communication, 1975). It is used extensively as a fumigant and there may be additional natural sources as discussed below.
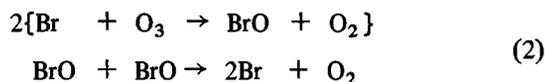
Bromine is present in both gas and particulate phases in the troposphere, with the gas phase dominant by a factor which ranges typically between 4 and 20. The mixing ratio of gaseous bromine is about 1.5×10^{-11} over Hawaii (Moyers and Duce, 1972) and it seems probable that the major constituent is HBr (see below). Measurements near the South Pole (Duce et. al., 1973) suggest values smaller by about a factor of 5. There are indications that the gaseous component is derived primarily from volatilization of bromine carried into the atmosphere as a component of marine aerosols (Duce et. al., 1963, 1965) with additional contributions from decomposition of CH_3Br and from particles released during the combustion of leaded gasoline (Moyers and Duce, 1972; Cadle, 1972; Martens et. al.,

1973). Using available data for the gasoline source strength, and empirical values for the atmospheric lifetime of HBr, we estimate a source strength for total gaseous bromine of 1.1×10^6 tons yr^{-1}, of which approximately 80% is derived from marine aerosols, 10% from CH_3Br, and 10% from automobiles.[†]

The importance of bromine in the stratosphere relates to its potential role as a catalyst for recombination of ozone. Catalysis can take place either through

$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + O \rightarrow Br + O_2 \tag{1}$$

or through

$$2\{Br + O_3 \rightarrow BrO + O_2\}$$
$$BrO + BrO \rightarrow 2Br + O_2 \tag{2}$$

The sequence (1) is equivalent to

$$O + O_3 \rightarrow 2O_2 \tag{1'}$$

The sequence (2) is equivalent to

$$O_3 + O_3 \rightarrow 3O_2 \tag{2'}$$

Reaction (2) could evolve Br_2 rather than Br. The efficiency of the cycle would not be greatly affected by uncertainties in the identity of the bromine product, since Br_2 will photolyse rapidly in the presence of sunlight.

Chlorine atom chains are terminated in the stratosphere by reactions with CH_4 and H_2, which tie up the gas in the relatively unreactive form HCl. The analogous reactions of bromine with CH_4 and H_2 are endothermic, and Watson (1975) was led to conclude that BrO might be the major form of gaseous bromine over an extensive height range. The efficiency of the catalytic cycles (1) and (2) could be exceedingly large in this case and mixing ratios of bromine as small as 10^{-12} would have appreciable effects on O_3.

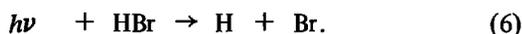It seems more likely however that HBr should dominate. Hydrogen bromide could be produced by

$$Br + HO_2 \rightarrow HBr + O_2 \tag{3}$$

and

$$Br + H_2O_2 \rightarrow HBr + HO_2 \tag{4}$$
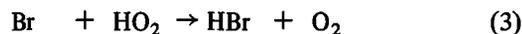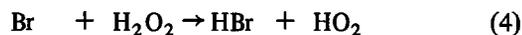
and would be removed by

$$OH + HBr \rightarrow H_2O + Br \tag{5}$$

with an additional contribution from

$$h\nu + HBr \rightarrow H + Br. \tag{6}$$

[†]The contribution from gasoline to the gaseous bromine budget of the northern hemisphere could be as large as 20%. In carrying out the computations summarized here we assumed a gasoline-related bromine source of 1.8×10^5 tons yr^{-1} (Klingman, 1974) and estimated that half of this bromine would be volatilized before removal from the atmosphere. We adopted a lifetime for inorganic gaseous bromine of 2 weeks, consistent with the analysis by Moyers and Duce (1972).

[†]Gaseous BrO could contribute to the "particulate" bromine found on neutral filters.

The chemical model adopted for this study, taken for the most part from Watson (1975), is given in Table 1.

Methyl bromide is removed by

$$OH + CH_3Br \rightarrow H_2O + CH_2Br. \qquad (7)$$
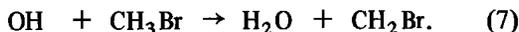
The bromine atom is subsequently released, and inorganic bromide (HBr + Br + BrO) is carried out of the lower atmosphere by rain as discussed earlier.

The major uncertainties in the chemical model relate to reactions (3) and (7), for which we adopt rate constants 10^{-11} cm^3 sec^{-1} and 2×10^{-12} exp (-1200/T) respectively. The rate for (3) was suggested by a consideration of high temperature data reported by Day et. al., (1971). The rate for (7) is consistent with preliminary measurements for the reaction at 300°K (Watson and Davis, 1975) and agrees also with the high temperature data by Wilson (1965).

Height profiles computed for major bromine species are given in Figure 1. The computations summarized by this and subsequent figures were carried out using procedures described elsewhere (McElroy et. al., 1974; Wofsy and McElroy, 1974; Wofsy et. al., 1975), with the eddy profile

taken from Hunten (1975), but multiplied by 1.5 above 16 km to obtain agreement with CH$_4$ observations. The chemical scheme allowed for 95 reactions, including those listed in Table 1. The flux of inorganic bromine at ground level was taken equal to 5.3×10^7 molecules cm^{-2} sec^{-1}‡ and the flux of CH$_3$Br was adjusted to agree with Lazrus et. al., (1975). The surface flux of CH$_3$Br was estimated in this manner at 3.0×10^6 molecules cm^{-2} sec^{-1}, approximately four times the value we inferred from Klingman (1974) for the net amount of bromine consumed in the manufacture of CH$_3$Br during 1974. Plonka (private communication, 1975) is of the opinion that only 25% of the industrial CH$_3$Br is released to the atmosphere, mainly as a byproduct of fumigation.

---

‡This value is the flux derived from a calculation using the washout profile given in Table 1, a mean ground-level mixing ratio of 1×10^{-11}, and Hunten's (1975) eddy diffusion profile.

†Burreson et al, (1975) reported very recently that CHBr$_3$ is an important component of certain seaweeds. If released to the atmosphere, CHBr$_3$ would play a role analogous to that attributed to marine CH$_3$Br in the present context.

Table 1

Reaction	Rate Expression[a]	Reference
k_1 Br + O$_3$ → BrO + O$_2$	$1.2 \times 10^{-12}(300°K)$ 1×10^{-10} exp (-1320/T) [A,C] 2.5×10^{-11} exp (-900/T) [B]	Watson (1975)
k_2 NO + BrO → NO$_2$ + Br	2×10^{-11}	Watson (1975)
k_3 Br + HO$_2$ → HBr + O$_2$	1×10^{-10} [C] 1×10^{-11} [B] 0. [A]	Day et. al., (1971) (see text)
k_4 BrO + O → Br + O$_2$	8×10^{-11}	Watson (1975)
k_5 BrO + BrO → 2Br + O$_2$	6.4×10^{-12}	Watson (1975)
BrO + $h\nu$ → Br + O	rate unknown in the atmosphere, probably slower than k_2 according to Watson (1975)	
k_6 OH + HBr → H$_2$O + Br	3.7×10^{-11} exp (-600/T)	Watson (1975)
k_7 OH + CH$_3$Br → H$_2$O + CH$_2$Br (c)	2×10^{-12} exp (-1200/T) 5.5×10^{-12} exp (-1900/T)	(see text) (see text)
k_8 Br + H$_2$O$_2$ → HBr + HO$_2$	1×10^{-11} exp (-1200/T)	(see text)
J_1 HBr + $h\nu$ → H + Br (b)	$0, 0, 2.8 \times 10^{-9}, 4.9 \times 10^{-6}$, $3.8 \times 10^{-6}, 6.7 \times 10^{-6}$	Romand and Vodar (1948)
J_2 CH$_3$Br + $h\nu$ → CH$_3$ + Br	$0, 0, 2.2 \times 10^{-9}, 4.1 \times 10^{-8}$, 7.3×10^{-6} 1.8×10^{-5}	Davidson (1951)
R_1 HBr + rain, aerosol → removed from atmosphere	1.7×10^{-6} $\quad$ 0 ≤ Z ≤ 4 km 8.5×10^{-7} $\quad$ 4 km < Z < 6 km 4.3×10^{-7} $\quad$ 6 km < Z < 8 km 1.7×10^{-7} $\quad$ 8 km < Z < 10 km 0 $\qquad\quad$ 10 km < Z	(see text)
k_g O + HBr → OH + Br	4.0×10^{-12} exp (-1360/T)	Brown and Smith (1975)

[a]Units are cm^3 sec^{-1}. Letters A, B, C refer to curves in Figure 2.

[b]Photodissociation rate is given as a function of altitude (in km), units of sec^{-1} (0, 10, ... , 50 km). A 24 hour average is used at 30° latitude, 0° solar declination.

[c]Br atom assumed released during subsequent chemistry of CH$_2$Br.
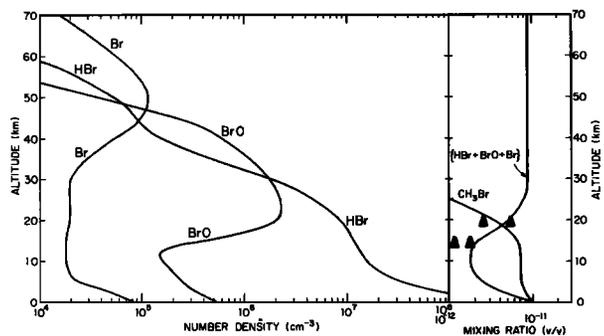
Figure 1: Height profiles for Br, HBr, BrO, and (Br + HBr + BrO): The data (△) are from Lazrus et. al., (1975). Computations allow for transport of N_2O, NO_X, CH_4, CO, O_3, (HBr + Br + BrO) and CH_3Br, and accounted for complete HO_X and NO_X chemistry. The mean lifetime calculated for CH_3Br (column concentration/flux) is 1.1 yr.

Taken at face value, the analysis given here implies both natural and industrial sources of CH_3Br. The sea is the most probable natural source, providing 75-95% of the CH_3Br shown in Figure 1.† We cannot however exclude the possibility of additional anthropogenic contributions to stratospheric bromine, associated for example with the escape of $(CH_2Br)_2$ from gasoline storage tanks or with the production of relatively insoluble bromine species during the combustion of leaded gasoline.

According to the model, the mixing ratio of inorganic bromine decreases by only a factor of 5 between ground and tropopause. This profile results from the choice of heterogeneous loss coefficient (cf. Wofsy et al., 1972), and is consistent with observational data for other soluble species, HCl (Farmer, 1975), NH_3 (Georgii and Muller, 1974) and HNO_3 (Lazrus et. al., 1974), and in agreement also with radioactivity removal rates summarized by Junge (1963).

The results in Figure 1 imply a reduction of magnitude 0.3% in the global concentration of O_3 due to bromine catalysis, of which approximately 0.2% may be attributed to
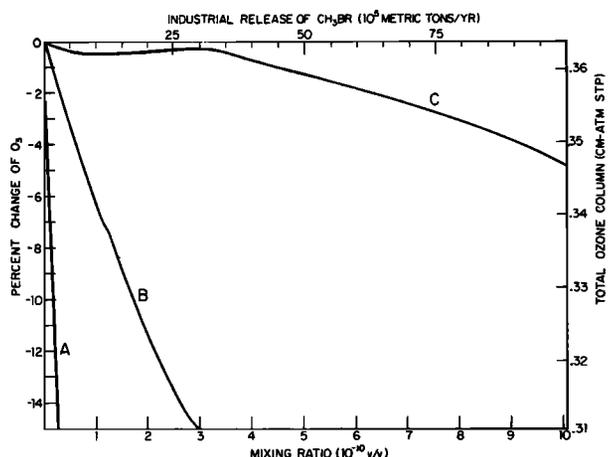
Figure 2: Ozone reduction as a function of (HBr + Br + BrO). Different curves refer to different combinations of rate expressions for k_3 and k_1, as shown in Table 1. Curve B combines "best estimates" for these rates Curve A shows model where HBr formation does not occur (k_3 and k_8 set to zero). Curve C illustrates the effect of a choice for k_3 and k_1 designed to minimize the ozone perturbation. The upper axis shows the approximate industrial release rate of CH_3Br which would produce the given stratospheric perturbation, using $k_7 = 2 \times 10^{-12} \exp(-1200/T)$.
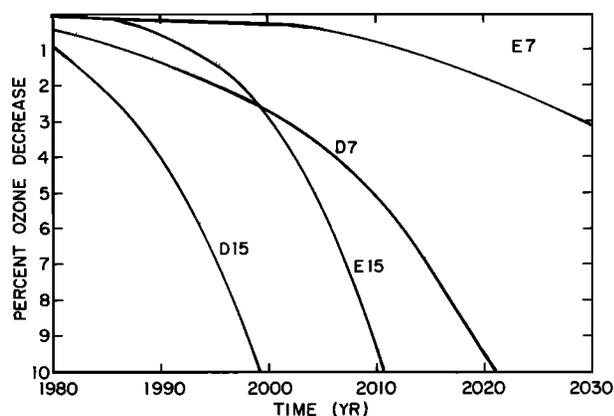
Figure 3: Reduction in ozone due to release of anthropogenic CH_3Br. Curves D and E differ in the values assumed for k_7: D, same rate as CH_4; E, preliminary measurement reported by Watson and Davis (1975). Other rates are the same as curve B, Figure 2. Seven and fifteen per cent annual increases are modelled by D7, E7, and D15, E15 respectively. The anthropogenic release was set equal to 10^4 tons in 1974, approximately 50% of the total global production. The release rate estimated by Plonka (see text) would imply a shift of the time axis by approximately 10 years for D7 and E7, 5 years for D15 and E15.

CH_3Br and 0.02% to bromine release from auto exhausts. Reductions in O_3, computed with various values for k_1 and k_3, are shown in Figure 2. The results in Figure 2 were derived subject to the constraint of a height independent value for the mixing ratio of HBr + Br + BrO, and illustrate the dependence of the computed ozone deficit on this parameter.

Figure 3 gives several conceivable time profiles for the ozone deficit associated with agricultural use of CH_3Br. Curves D and E differ in choice of rate constant for reaction of OH with CH_3Br. Curve E employs the value suggested by analogy with the $OH-CH_3Cl$ reaction and is consistent also with the preliminary measurement by Watson and Davis. Curve D uses the $OH-CH_4$ reaction rate. Production and use of CH_3Br is assumed to grow in curves D7 and E7 at a rate of 7% per annum, a value close to the historical trend. Curves D15 and E15 envisage a somewhat larger growth rate, approximately 15% per annum. A growth rate of this magnitude may not be unreasonable however, since cost factors currently limit fumigation to a very few high value crops. Approximately 10% of world bromine production is used in the manufacture of CH_3Br, with roughly 63% employed in the production of ethylene dibromide.

It seems clear that an unconstrained growth in the use of methyl bromide could cause future problems for ozone. Measurements of bromine compounds in the atmosphere, together with laboratory studies of several key reactions, notably k_1, k_3 and k_7, should be pursued in order to clarify these matters.

Acknowledgements

References

Brown, F.D.H. and I.W.M. Smith, Absolute rate constants for the reactions of $O(^3P)$ atoms with HCl and HBr, *Int. J. Chem. Kin.*, *7*, 301, 1975.

Burreson, B.J. and R.E. Moore, Haloforms in essential oil of the alga *A. Taxiformis, Tetrahedron Lett.*, *7*, 473, 1975.

Cadle, R.D., Composition of the stratospheric "sulfate" layer, *Trans. of Am. Geophys. U.*, *53*, p. 812, 1972.

Crutzen, P.J., SST's, a threat to the earth's ozone shield, *Ambio, 1*, p. 41, 1972.

Davidson, N., The ultraviolet absorption spectra and the refractive indices of some fluorobromomethanes, *J. Am. Chem. Soc.*, *73*, p. 468, 1951.

Day, M.J., D.V. Stamp, K. Thompson, and G. Dixon-Lewis, Inhibition of hydrogen-air and hydrogen-nitrous oxide flames by halogen compounds, *13th Comb. Symp.*, p. 705, 1971.

Delany, A.C., J.P. Shedlovsky, and W.H. Pollock, Stratospheric aerosol: the contribution from the troposphere, *J. Geophys. Res.*, *79*, p. 5646, 1974.

Duce, R.A., J.T. Wasson, J.W. Winchester, and F. Burns, Atmospheric iodine, bromine and chlorine, *J. Geophys. Res.*, *68*, p. 3943, 1963.

Duce, R.A., J.W. Winchester, and T.W. Van Nahl, Iodine, bromine and chlorine—the Hawaiian marine atmosphere, *J. Geophys. Res.*, *70*, p. 1775, 1965.

Duce, R.A., W H. Zoller, and J.L. Moyers, Particulate and gaseous halogens in the Antarctic atmosphere, *J. Geophys. Res.*, *78*, p. 7802, 1972.

Farmer, C.B., CIAP Conference, Cambridge, Mass., 1975.

Georgii, H.W., and W.J. Müller, On the distribution of ammonia in the middle and lower troposphere, *Tellus XXVI 1-2*, p. 180, 1974.

Hunten, D.M., Philosophy of one-dimensional modelling, 4th CIAP Conference, Cambridge, Mass., 1975.

Johnston, H.S., Reduction of stratospheric ozone by nitrogen oxide catalysts from SST exhaust, *Science, 173*, p. 517, 1971.

Junge, C.E., *Air Chemistry and Radioactivity*, p. 298ff, Academic Press, New York, New York, 1963.

Klingman, C.L., U.S. Bureau of Mines *Mineral Yearbook*, U.S. Dept. of the Interior, 1974.

Lazrus, A., B. Gandrud, R. Woodard, and W. Sedlacek, Measurements of stratospheric halogens and nitric acid, paper presented at CIAP Conference, Cambridge, Mass., 1975.

Martens, C.S., J.J. Wesolowski, R. Kaifer, and W. John, Lead and bromine particle size distribution in San Francisco Bay area, *Atmospheric Environment, 7*, p. 905, 1973.

McElroy, M.B., S.C. Wofsy, J.E. Penner, and J.C. McConnell, Atmospheric Ozone: possible impact of stratospheric aviation, *J. Atmos. Sci., 31*, p. 287, 1974.

Molina, M.J., and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, *Nature, 249*, p. 810, 1974.

Moyers, J.L. and R.A. Duce, Gaseous and particulate Iodine in the marine atmosphere, *J. Geophys. Res., 77*, p. 5229, 1972.

Romand, J., and B. Vodar, Spectre d'absorption de l'acide chlorohydrique gazeux dans la région de Schumann, *C.R. (Acad. Sci.), 226*, p. 238, 1948.

Watson, R.T., Chlorine, the chlorine oxides and other halogen species, CIAP Monograph, vol. 1, to be published.

Watson, R.T., and D.D. Davis, Meeting of the Am. Chemical Soc., Philadelphia, Pa., April 9, 1975.

Wilson, W.E., Structure, kinetics, and mechanism of a methane-oxygen flame inhibited with methyl bromide, *10th Comb. Symp.*, p. 47, 1965.

Wofsy, S.C., J.C. McConnell and M.B. McElroy, Atmospheric CH_4, CO and CO_2, *J. Geophys. Res.*, *77*,4477, 1972.

Wofsy, S.W. and M.B. McElroy, HO_X, NO_X, and ClO_X: their role in atmospheric photochemistry, *Can. J. Chem., 52*, p. 1582, 1974.

Wofsy, S.W., M.B. McElroy, and N.D. Sze, Freon consumption: implications for atmospheric ozone, *Science,187*, p. 535, 1975.