

## THE CHEMISTRY OF ATMOSPHERIC BROMINE

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**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.

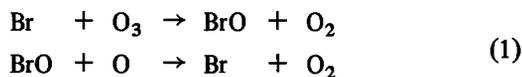
The chemistry of atmospheric ozone may be influenced to a remarkable extent by exceedingly small quantities of select stratospheric gases. Attention has focused in recent years on nitric oxide released by SST's (Johnston, 1971; Crutzen, 1972) and on chlorine produced by photodecomposition of chlorofluoromethanes (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.

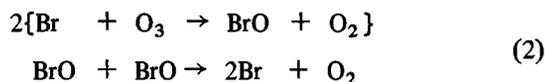
Bromine is present in both gas and particulate phases in the troposphere, with the gas phase dominant by a factor which ranges typically between 4 and 20. The mixing ratio of gaseous bromine is about  $1.5 \times 10^{-11}$  over Hawaii (Moyers and Duce, 1972) and it seems probable that the major constituent 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  $1.1 \times 10^6$  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



or through



The sequence (1) is equivalent to



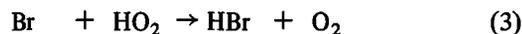
The sequence (2) is equivalent to



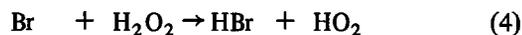
Reaction (2) could evolve  $Br_2$  rather than Br. The efficiency of the cycle would not be greatly affected by uncertainties in the identity of the bromine product, since  $Br_2$  will photolyse rapidly in the presence of sunlight.

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



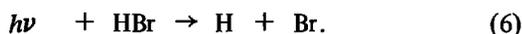
and



and would be removed by



with an additional contribution from

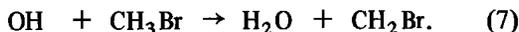


†The contribution from gasoline to the gaseous bromine budget of the northern hemisphere could be as large as 20%. In carrying out the computations summarized here we assumed a gasoline-related bromine source of  $1.8 \times 10^5$  tons  $yr^{-1}$  (Klingman, 1974) and estimated that half of this bromine 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



The bromine atom is subsequently released, and inorganic bromide ( $\text{HBr} + \text{Br} + \text{BrO}$ ) 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  $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  and  $2 \times 10^{-12} \exp(-1200/T)$  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  $300^\circ\text{K}$  (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 Huntten (1975), but multiplied by 1.5 above 16 km to obtain agreement with  $\text{CH}_4$  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  $5.3 \times 10^7 \text{ molecules cm}^{-2} \text{ sec}^{-1}$ † and the flux of  $\text{CH}_3\text{Br}$  was adjusted to agree with Lazrus et al., (1975). The surface flux of  $\text{CH}_3\text{Br}$  was estimated in this manner at  $3.0 \times 10^6 \text{ molecules cm}^{-2} \text{ sec}^{-1}$ , approximately four times the value we inferred from Klingman (1974) for the net amount of bromine consumed in the manufacture of  $\text{CH}_3\text{Br}$  during 1974. Plonka (private communication, 1975) is of the opinion that only 25% of the industrial  $\text{CH}_3\text{Br}$  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  $1 \times 10^{-11}$ , and Huntten's (1975) eddy diffusion profile.

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

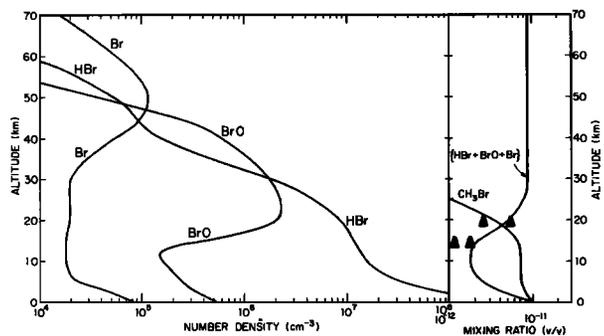
Table 1

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

<sup>a</sup>Units are  $\text{cm}^3 \text{ sec}^{-1}$ . Letters A, B, C refer to curves in Figure 2.

<sup>b</sup>Photodissociation rate is given as a function of altitude (in km), units of  $\text{sec}^{-1}$  (0, 10, ..., 50 km). A 24 hour average is used at  $30^\circ$  latitude,  $0^\circ$  solar declination.

<sup>c</sup>Br atom assumed released during subsequent chemistry of  $\text{CH}_2\text{Br}$ .

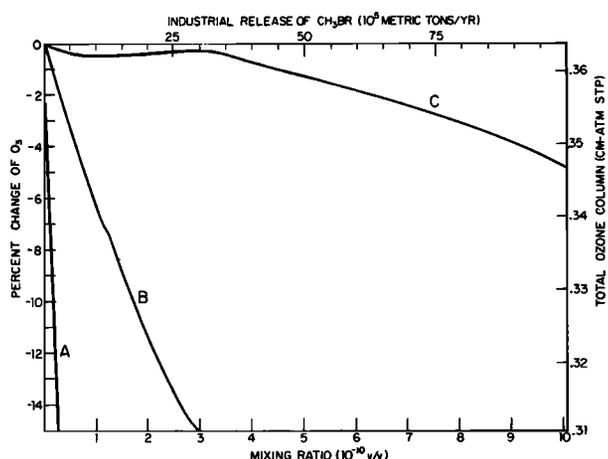


**Figure 1:** Height profiles for Br, HBr, BrO, and (Br + HBr + BrO): The data ( $\Delta$ ) are from Lazrus et. al., (1975). Computations allow for transport of  $N_2O$ ,  $NO_x$ ,  $CH_4$ ,  $CO$ ,  $O_3$ , (HBr + Br + BrO) and  $CH_3Br$ , and accounted for complete  $HO_x$  and  $NO_x$  chemistry. The mean lifetime calculated for  $CH_3Br$  (column concentration/flux) is 1.1 yr.

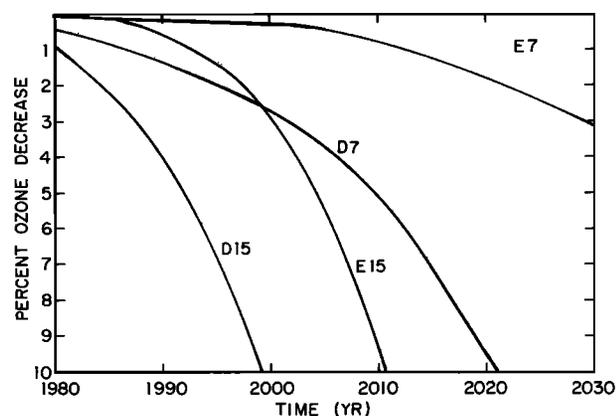
Taken at face value, the analysis given here implies both natural and industrial sources of  $CH_3Br$ . The sea is the most probable natural source, providing 75-95% of the  $CH_3Br$  shown in Figure 1.† We cannot however exclude the possibility of additional anthropogenic contributions to stratospheric 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.

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