

Upper Limits for the Rate Coefficients for Reactions of BrO with Formaldehyde and HBr

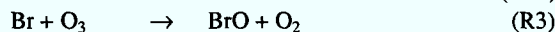
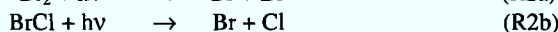
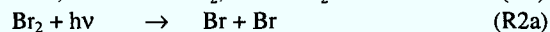
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Abstract. The reactions of the BrO radical with hydrogen bromide, $\text{BrO} + \text{HBr} \rightarrow \text{HOBr} + \text{Br}$ (R4) and with HCHO, $\text{BrO} + \text{HCHO} \rightarrow \text{HOBr} + \text{HCO}$ (R5) have been studied at 298 K, 1 atm. pressure in an environmental chamber. No conclusive evidence for the occurrence of either reaction was found and upper limits for both reaction rate coefficients are reported ($k_4, k_5 < 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). These upper limits are about 4-5 times lower than recent estimates [Hansen *et al.*, 1999a,b].

Introduction

The episodic removal of surface layer O_3 in polar regions in the spring is now a well-documented phenomenon [e.g., Oltmans, 1981; Barrie *et al.*, 1988, 1994; Bottenheim *et al.*, 1990; Shepson *et al.*, 1996]. It is generally accepted that this O_3 depletion results from reactions involving Br [e.g., Barrie *et al.*, 1988, 1994; Bottenheim *et al.*, 1990; Hausmann and Platt, 1994; Jobson *et al.*, 1994; Shepson *et al.*, 1996; Ramacher *et al.*, 1997, 1999; Ariya *et al.*, 1998; Rudolph *et al.*, 1999; Impey *et al.*, 1999], with condensed-phase chemistry likely playing a key role. Critical to the generation of large fluxes of reactive gas phase Br-atoms appears to be the condensed-phase reaction between HOBr and halide ions, leading to gas-phase BrCl and Br_2 :



Thus, it is clear that reactions involving HOBr and HBr may have a significant effect on the rate of O_3 depletion. Recently, the occurrence of two reactions involving these species has been suggested [Hansen *et al.*, 1999a,b; Michalowski *et al.*, 2000],



and a combination of theory and experiment has been used to estimate rate coefficients of order $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Hansen *et al.*, 1999a,b]. Both reactions are exothermic by $\approx 9 \text{ kcal/mole}$ [DeMore *et al.*, 1997; Hansen *et al.*, 1999a,b] and are thus plausible. However, an upper limit of $6.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has previously been reported [Turnipseed *et al.*, 1991] for (R4), and a reaction analogous to (R5) between ClO

and HCHO has also been shown to be very slow [Poulet *et al.*, 1980], $k < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Modeling studies have also been conducted [Michalowski *et al.*, 2000] to investigate the potential impact of these reactions. While (R4) has no effect on the rate of O_3 depletion or on Br partitioning (R5) is potentially important in driving the conversion of BrO to HOBr and thus in enhancing the rate of (R1) and the overall rate of O_3 depletion [Michalowski *et al.*, 2000]. The reaction could also be important in generating high gas-phase HOBr levels that are consistent with observation [Impey *et al.*, 1999]. Due to the potential impact of (R5) and the lack of a direct experimental study of its rate coefficient, studies of this reaction (as well as (R4)) have been carried out in an environmental chamber. Upper limits for both k_4 and k_5 are reported.

Experimental

The environmental chamber / Fourier transform spectrometer system used in these studies has been described elsewhere [Shetter *et al.*, 1987]. The chamber is constructed of stainless steel, and has a total volume of 47 L. Infrared spectra were obtained over the range $800\text{--}3900 \text{ cm}^{-1}$ at a spectral resolution of 1 cm^{-1} from the co-addition of 50-150 interferograms.

Studies of (R4) were conducted by photolyzing mixtures of Br_2 and O_3 in 1 atm synthetic air, with HBr added in some experiments. For the study of (R5), reaction mixtures made up of Br_2 and HCHO in 1 atm O_2/N_2 were photolyzed, with O_3 added in some cases. Photolyses were conducted using a filtered Xe-arc lamp, $\lambda > 410 \text{ nm}$. In this way, Br_2 was photolyzed efficiently (rate coefficient of $3.0 \pm 0.5 \times 10^{-3} \text{ s}^{-1}$), while other trace species in the chamber (O_3 , HBr, HCHO) were not photolyzed to any measurable extent. Trace species (Br_2 , HCHO, O_3 , HBr) were added to the chamber from smaller calibrated volumes, while O_2 was added directly to the chamber. Experiments were conducted by irradiating the reaction mixtures for a measured time (5-45 s), with an IR spectrum recorded following each irradiation. Quantification of HCHO, O_3 , HBr, HCOOH, and CO (detection limits in the range $0.5\text{--}3 \times 10^{12} \text{ molecule cm}^{-3}$) was accomplished by comparison of IR spectra with standard spectra recorded in our laboratory, while $[\text{Br}_2]$ in the chamber was calculated from the pressure measured in the calibrated volume. O_3 was generated by flowing UHP O_2 through an electrical discharge at ambient pressure, and collecting the effluent in a 1-L bulb. O_3 mixing ratios in the bulb, as determined by UV absorption, were $3.8 \pm 0.4\%$. O_3 mixing ratios in the chamber, quantified using known IR absorption cross sections [Uselman *et al.*, 1979] were found to be 80-100% of the amount anticipated based on the UV determination of the bulb contents; for modeling purposes, the concentration determined by IR absorption was used. Other gases used in this study were obtained from commercial sources.

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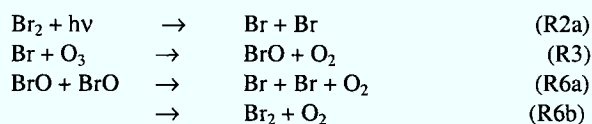
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Rate coefficients for (R4) and (R5) were extracted from the data via simulation of the reaction systems, conducted using Acuchem [Braun *et al.*, 1988]. The reactions included in the model, the rate coefficients used, and the source of the rate coefficient data are given in Table 1. For studies of k_4 , only (R2a), (R3), (R4) and (R6) play a role. For k_5 , although the full model was employed in the analysis, OH chemistry is of little significance and only (R2), (R3), and (R5)-(R10) are important. As determined by sensitivity studies, the reported upper limits take into account uncertainties [DeMore *et al.*, 1997] in the rate coefficients used in the model.

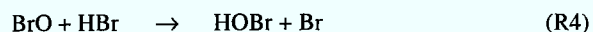
Results and Discussion

The value of k_4 was obtained by monitoring the rate of O_3 depletion in the cw photolysis of Br_2 in the presence of O_3 , O_2 and N_2 , with and without HBr added. In the absence of HBr, the following reactions play an important role:



Thus, O_3 is depleted via a catalytic reaction sequence involving Br atoms, with the chain length (CL, number of O_3 molecules

destroyed per Br produced in R2a) given by the relative rate coefficients for (R6a) and (R6b), $k_{6a}/k_{6b} = 5.7 \pm 1.0$ [DeMore *et al.*, 1997]. Addition of HBr to the reaction mixtures will be important if (R4)



is sufficiently rapid to enhance the chain length: $CL = \{2 k_{6a} [BrO] + k_4 [HBr]\} / 2 k_{6b} [BrO]$.

Typical O_3 data as a function of photolysis time are shown in Figure 1. In this set of experiments (conducted in succession over a 1 hr period), Br_2 (2.1×10^{14} molecule cm^{-3}) was photolyzed in the presence of O_3 (1.0×10^{15} molecule cm^{-3}), O_2 (560 Torr) and N_2 (140 Torr) with HBr present in two cases (0, 7, 14, and 0×10^{14} molecule cm^{-3}). The "zero HBr" experiment was repeated to ensure that the Br_2 photolysis rate had not changed over the course of the measurements. During the course of this study, a heterogeneous reaction between HBr and O_3 was noted, with an apparent rate coefficient of 8×10^{-18} cm^3 molecule $^{-1}$ s $^{-1}$ in the illuminated chamber, and the O_3 loss data from these four experiments have been corrected for the occurrence of this reaction. It is apparent from Figure 1 that no significant change in the rate of O_3 depletion occurs upon addition of HBr, once the heterogeneous processes are accounted for. Also shown in Figure 1 are the results of box model simulations (with $[HBr] = 0$ or $14 \times$

Table 1. Reaction mechanism and rate coefficients used in model simulations

Reaction		Rate Coefficient (cm^3 molecule $^{-1}$ s $^{-1}$)	Reference	Reaction Number
$Br_2 + h\nu$	$\rightarrow$ $Br + Br$	$(3.1 \pm 0.4) \times 10^{-3}$ s $^{-1}$	measured	(R2a)
$Br + O_3$	$\rightarrow$ $BrO + O_2$	1.2×10^{-12}	a	(R3)
$BrO + HBr$	$\rightarrow$ $Br + HOBr$	varied		(R4)
$BrO + HCHO$	$\rightarrow$ $HOBr + HCO$	varied		(R5)
$BrO + BrO$	$\rightarrow$ $Br + Br + O_2$	2.7×10^{-12}	a	(R6a)
	$\rightarrow$ $Br_2 + O_2$	4.8×10^{-13}	a	(R6b)
$Br + HCHO$	$\rightarrow$ $HCO + HBr$	1.1×10^{-12}	a	(R7)
$HCO + O_2$	$\rightarrow$ $HO_2 + CO$	5.5×10^{-12}	a	(R8)
$HO_2 + HO_2$	$\rightarrow$ $H_2O_2 + O_2$	3.0×10^{-12}	a	(R9)
$BrO + HO_2$	$\rightarrow$ $HOBr + O_2$	2.0×10^{-11}	a	(R10)
$Br + HO_2$	$\rightarrow$ $HBr + O_2$	2.0×10^{-12}	a	(R11)
$HO_2 + O_3$	$\rightarrow$ $OH + O_2 + O_2$	2.0×10^{-15}	a	(R12)
$OH + O_3$	$\rightarrow$ $HO_2 + O_2$	6.8×10^{-14}	a	(R13)
$OH + HCHO$	$\rightarrow$ $HCO + H_2O$	1.1×10^{-11}	a	(R14)
$OH + HO_2$	$\rightarrow$ $H_2O + O_2$	1.1×10^{-10}	a	(R15)
$OH + BrO$	$\rightarrow$ $Br + HO_2$	7.0×10^{-11}	a	(R16)
$OH + Br_2$	$\rightarrow$ $HOBr + Br$	4.2×10^{-11}	a	(R17)
$OH + HBr$	$\rightarrow$ $Br + H_2O$	1.1×10^{-11}	a	(R18)
$OH + CO + O_2$	$\rightarrow$ $HO_2 + CO_2$	2.4×10^{-13}	a	(R19)
$OH + H_2O_2$	$\rightarrow$ $HO_2 + H_2O$	1.7×10^{-12}	a	(R20)
$OH + HOBr$	$\rightarrow$ $BrO + H_2O$	$< 5 \times 10^{-13}$	b	(R21)
$HO_2 + HCHO$	$\rightarrow$ $HOCH_2OO$	8×10^{-14}	c	(R22)
$HOCH_2OO + M$	$\rightarrow$ $HO_2 + HCHO$	37	d	(R23)
$2 HOCH_2OO$	$\rightarrow$ $2 HOCH_2O + O_2$	2.8×10^{-12}	e,a	(R24)
$HOCH_2O + O_2$	$\rightarrow$ $HCOOH + HO_2$	2×10^{-15}	e,a	(R25)
$HOCH_2OO + HO_2$	$\rightarrow$ $HOCH_2OOH + O_2$	5×10^{-12}	e,a	(R26)
$HOCH_2OO + BrO$	$\rightarrow$ $HOCH_2O + Br + O_2$	6×10^{-12}	e,f	(R27)
$HOCH_2OO + Br$	$\rightarrow$ $HOCH_2O + BrO$	4.4×10^{-13}	e,g	(R28)

^aDeMore *et al.*, 1997

^bKukui *et al.*, 1996

^cAtkinson *et al.*, 1997

^dVaried to match observed HCOOH levels

^eBy analogy to reactions of CH_3O_2 or CH_3O

^fAranda *et al.*, 1997

^gAranda *et al.*, 1998

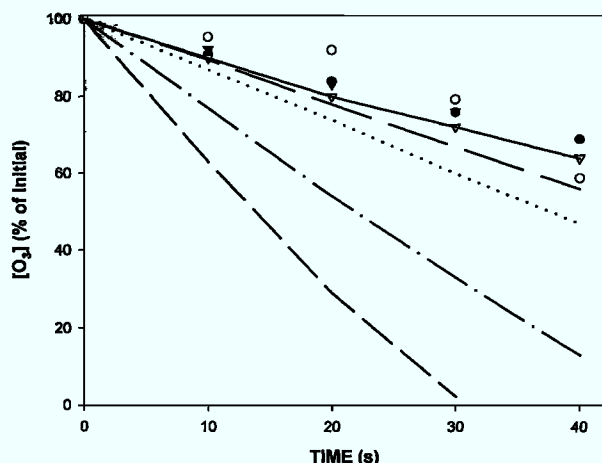


Figure 1. Concentration of O_3 (% of initial) as a function of time in the photolysis of mixtures of Br_2 (2.1×10^{14} molecule cm^{-3}), O_3 (1.0×10^{15} molecule cm^{-3}), O_2 (560 Torr) and N_2 (140 Torr). Data for $[HBr] = 0, 7, 14,$ and 0×10^{14} molecule cm^{-3} are given by solid circles, solid triangles, open circles, and open triangles respectively. Lines are results of box model simulations: Solid line, $k_4 = 0$; long dashed line, $k_4 = 1.5 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$; dotted line, $k_4 = 3 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$; dash-dot line, $k_4 = 1 \times 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$; short dashed line, $k_4 = 2.1 \times 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$.

10^{14} molecule cm^{-3}) for a variety of values for k_4 . Clearly, the data/model comparison shows that the rate coefficient for (R4) is quite small; in fact, there is no evidence for its occurrence in the data. Even if the heterogeneous reaction is not accounted for and the excess loss of O_3 in the presence of HBr is attributed to the occurrence of (R4), a maximum value of $k_4 = 4 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$ can be derived. Numerous experiments similar to those just described were conducted, with similar results, and a conservative upper limit of $k_4 \leq 4 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$ is reported.

In a couple of experiments with HBr present (though not in most), small amounts of HOBr (near the detection limit) were observed, providing possible evidence for the occurrence of (R4). As determined from simulations, the amount of HOBr (determined using IR band strength data from Lee [1995]) was consistent with a value for k_4 of no more than 1×10^{-15} cm^3 molecule $^{-1}$ s $^{-1}$. However, given the uncertainties in the bandstrength data for HOBr, and the sporadic nature of the HOBr observations, we choose to quote the more conservative upper limit, $k_4 < 4 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$, which is based on the O_3 loss data.

The upper limit obtained here is similar to that reported by Turnipseed *et al.* [1991], who studied the reaction in a discharge flow / mass spectrometer system, and is somewhat slower than the value calculated by Hansen *et al.*, [1999b] using transition state theory. Our result, coupled with the model results of Michalowski *et al.* [2000] (which showed no enhancement of the rate of O_3 depletion even with $k_4 = 2.1 \times 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$), show that this reaction is of no significance in boundary layer O_3 depletion. The contribution of this reaction to either HBr destruction or HOBr formation in the stratosphere can also be ruled out [Turnipseed *et al.*, 1991].

Experiments to determine the value of the rate coefficient for (R5) involved monitoring the rate of disappearance of HCHO in the photolysis of Br_2 / HCHO / O_2 / N_2 mixtures, in the presence and absence of added O_3 . In the absence of O_3 , each Br atom

produced in the photolysis of Br_2 reacts with HCHO and, to a first approximation, one HCHO is consumed per Br produced. In fact, this type of experiment is used to determine the Br_2 photolysis rate in the chamber. Upon addition of O_3 , some Br atoms are converted to BrO via (R3). If there is no reaction between BrO and HCHO, this provides a means for loss of reactive Br species through the self-reaction of BrO (R6b) and through reaction of BrO with HO_2 (R10) and the loss rate of HCHO is reduced. However, if a significant reaction does occur between BrO and HCHO, the production of BrO ceases to provide a pathway for termination and the rate of HCHO depletion approaches that observed in the absence of O_3 .

A complication arises from the consumption of HCHO via reaction with HO_2 , (R22)-(R28) of Table 1, which accounted for 15-30% of the HCHO loss. Though rate coefficients for these reactions have in many cases not been measured, those estimated in Table 1 were capable of reproducing the observed $[HCOOH]$ and $[CO]$ to within $\pm 7\%$ of the observed values. The details of the HO_2 /HCHO reaction are not important in arriving at the k_5 value reported below.

Typical experimental data are shown in Figure 2. Here, $[HCHO]$ is plotted (in % of initial concentration) as a function of photolysis time in back-to-back experiments involving the photolysis of Br_2 (2.2×10^{14} molecule cm^{-3}), HCHO (6.9×10^{14} molecule cm^{-3}), O_2 (152 Torr), N_2 (555 Torr) mixtures, conducted with O_3 (2.6×10^{15} molecule cm^{-3}) and without O_3 present. As can readily be seen, the rate of HCHO consumption is decreased substantially upon addition of O_3 , indicating that a fast reaction between HCHO and BrO cannot be occurring. Also shown in the Figure are results of box model simulations using various values for k_5 . Clearly, the data do not support a rate coefficient of $\approx 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$ as reported by Hansen *et al.* [1999a], though a rate coefficient of order 1.5×10^{-15} cm^3 molecule $^{-1}$ s $^{-1}$ cannot be ruled out. Other experiments conducted in a similar fashion provided similar results. In no case was a value for k_5 of greater

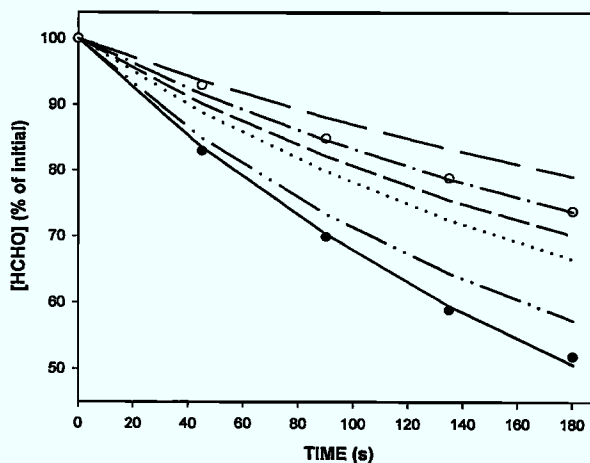


Figure 2. Concentration of HCHO (% of initial) as a function of time in the photolysis of mixtures of Br_2 (2.2×10^{14} molecule cm^{-3}), HCHO (6.9×10^{14} molecule cm^{-3}), O_2 (152 Torr) and N_2 (555 Torr), with $[O_3] = 0$ (closed circles) or 2.6×10^{15} molecule cm^{-3} (open circles). Also shown are results of box model simulations: Solid line, no O_3 , $k_5 = 0$; long dashed line, O_3 present, $k_5 = 0$; dash-dot line, O_3 present, $k_5 = 1.5 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$; short dashed line, O_3 present, $k_5 = 3 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$; dotted line, O_3 present, $k_5 = 5 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$; dash-dot-dot line, O_3 present, $k_5 = 1.5 \times 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$.

than $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ required to model the observed data, while in some cases no reaction was required. Given the uncertainties in the modeling of this relatively complex reaction mechanism, we report a conservative upper limit, $k_5 \leq 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The value of k_5 is probably even lower at temperatures encountered in the polar troposphere, as the reaction likely possesses a barrier [Hansen *et al.*, 1999a]. The low value of k_5 is also consistent with the findings of Poulet *et al.* [1980] who, using a discharge flow / EPR technique, reported an upper limit of $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate coefficient for reaction of ClO with HCHO, a reaction which possesses nearly the same energetics as (R5).

As alluded to earlier, the modeling studies of Michalowski *et al.* [2000] showed that (R5), if operative with a rate coefficient $k_5 = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, significantly enhances the rate of O_3 depletion in the polar troposphere and impacts the levels of HOBr present. Clearly, further modeling studies using the upper limit to k_5 determined here are warranted.

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