KINETICS OF THE REACTIONS OF ATOMIC BROMINE WITH HO2 AND H2O2

Jessica POSEY John SHERWELL and Myron KAUFMAN

Department of Chemistry Emory University Atlanta Georgia 30322 USA

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The room-temperature rate constant of Br + HO₂ is 2.2×10^{-12} cm³ molecule⁻¹ s⁻¹ while that of Br + H₂O₂ is less than 2×10^{-15} cm³ molecule⁻¹ s⁻¹. Arguing from correlations between activation energies and enthalpy changes of similar reactions, we conclude that HBr is a negligible reservoir for stratospheric bromine

1 Introduction

Although considerable publicity has been given to possible destruction of the stratospheric ozone layer by chlorine-containing compounds such as the chlorofluoromethanes much less attention has been paid to the analogous problem resulting from bromine-containing compounds [1-3] Presently, the anthropogenic stratospheric bromine burden is relatively small compared to that of chlorine. However important differences between the stratospheric chlorine and bromine cycles have been noted which might make bromine on a per-atom basis considerably more destructive to ozone than chlorine. Since tropospherically stable bromme compounds are finding increasing use in agriculture (CH_3Br) and fire control (CF_3Br), it appears wise to improve our knowledge of stratospheric bromine chemistry before additional industrial, agricultural and military commitment is made to the use and production of these compounds

In modeling stratospheric chemistry rate constants are required for many elementary reactions Since experimental data for reactions of Cl and ClO (ClOX) is more complete than that for Br and BrO (BrOX) rates of BrOX reactions have often been estimated as those of the analogous ClOX reactions In certain cases this procedure is clearly recognized as being in error For example, since Br + CH₄ and Br + H₂ are both ≈ 16 kcal endothermic, they are certainly much slower than Cl + CH₄ and Cl + H₂, which are essentially thermoneutral However, even for exothermic reactions there usually exists a correlation between activation energy and exothermicity [4,5] Such correlations predict that, even for exothermic reactions, reactions that form a hydrogen halide should be much slower for Br than for Cl, since they are driven by 16 kcal less enthalpy change This article deals with measurements of the rates of two such reactions, Br + H_2O_2 and Br + HO_2 These reactions are of considerable importance for stratospheric modeling, since they have been postulated as the primary means of converting BrOX to HBr [6], which is catalytically inactive for destroying stratospheric ozone

2. Experimental procedure and results

Rate constants are measured in a 34 mm i d pyrex flow reactor, ccated with halocarbon wax [7] which was fluorinated prior to use. Reactant concentrations are measured by a molecular beam analyzer [8,9], which operates as an ordinary mass spectrometer when monitoring diamagnetic molecules such as H_2O_2 When monitoring paramagnetic species such as Br and HO_2 , however, an obstacle blocks the direct path into the ionizer of the mass spectrometer, and a hexapolar electromagnet is used to "focus" paramagnetic components of the sampled beam into the ionizer

Bromine atoms are produced by a 2450 MHz discharge in dilute Br_2 —Ar or Br_2 —He mixtures In studying the Br + HO₂ reaction, the bromine atoms are added through a central 12 mm o d tube with an open end, as



Fig 1 Flow reactor (1) sampling cone, (B) inner tube supports (C) pyrev flow tube, (D) inner tube, (D) H_2O_2 inlet, (F) bubbler inlet, (G) H_2O_2 reservoir, (H) water bath, (I) inert gas inlet, (J) gas inlet (K) quartz discharge tube, (L) alumina discharge tube, (M) microwave cavities, (N) gas inlet, and (O) to pump

shown in fig 1 Although this arrangement is not optimum for rapid mixing of reagents, it does provide higher atom concentrations than does a closed tube with many small openings. The central tube is coated internally with phosphoric acid and externally with halocarbon wax. The position of the central tube in the flow tube is varied by sliding it through an O-ring seal. The discharge cavity on the central tube is fixed to the same sliding mount that holds the tube, so that the position of the tube can be varied without changing the tuning of the cavity and the flow of bromine atoms delivered at the end of the tube.

Bromme atom concentrations are taken as twice the decrease of the Br_2^+ ion signal upon initiating the discharge In addition, the bromme atom signal is calibrated by partially reacting a measured flow of Br_2 with atomic fluorine (generated by a 2450 MHz discharge on an $Ar-F_2$ mixture in an alumina discharge tube) ≈ 5 cm upstream of the sampling orifice It is assumed that each Br_2 destroyed in the reaction

$$\mathbf{F} + \mathbf{Br}_{2} \to \mathbf{BrF} + \mathbf{Br} \tag{1}$$

produces a bromine atom at the sampling orifice Bromine atoms have been found to react only very slowly with undischarged F_2 [10] This calibration method avoids possible reaction of the bromine atoms with the phosphoric acid coating on the intenor of the central tube. In general, Br concentrations determined from the Br₂ destroyed and from the calibrated atom signal agree to within 10%.

Atomic fluorine is mixed with excess H_2O_2 (generated by flowing Ar through >90% H_2O_2 solution, using an all glass and tefton inlet line) 40 cm upstream of the orifice, producing HO₂ radicals by the reactions

$$F + H_2O_2 \rightarrow HF + HO_2 \tag{2}$$

$$F + HO_2 \rightarrow HF + O_2, \tag{3}$$

$$HO_2 + riO_2 \rightarrow H_2O_2 + O_2 \tag{4}$$

Since it is difficult to reliably measure flows of H_2O_2 . due to the ease with which it is decomposed, the molecular beam analyzer is calibrated to measure absolute H_2O_2 and HO_2 concentrations by a two-step titration procedure First, fluorine atoms in excess are added to H₂O₂ A calibration factor for F atoms is obtained by reacting them with a measured flow of Br₂ in excess and measuring the diminution of the Bro signal With F in excess two fluorine atoms react with each $H_{-}O_{2}$ [independent of the occurrence of reaction (4)], directly providing the H_2O_2 calibration factor The fluorine atom concentration is then reduced, by reducing the flow of F_2 , until H_2O_2 is in excess, and all of the fluorine atoms are consumed. An HO₂ signal is then observed as magnetic focusing at m/e = 33. Since consumption of H₂O₂ requires two F atoms, except when the final product is HO2, when only a single F atom is required.

$$F_{\text{consumed}} = 2(H_2O_2)_{\text{consumed}} - (HO_2)_{\text{measured}}$$
(5)

Since the instrument is now calibrated for absolute [F] and $[H_2O_2]$, a calibration factor for the HO₂ signal is obtained. Measurements of absolute HO₂ concentrations are useful in determining that conditions for pseudo-first-order kinetics are achieved, with [Br] \geq [HO₂] Actual determinations of rate constants, however, are performed using only relative HO₂ concentrations

The rate constant of the Br + HO₂ reaction was measured as $[Br]^{-1} d \ln ([HO_2]_{off}/[HO_2]_{on})/dt$, in a series of runs in which [Br]-to- $[HO_2]_{initial}$ ratios were 5-50 By plotting the ratio of the HO₂ signal with the Br₂ discharge off and on, the self-decay of HO₂ radicals is accounted for under identical pressure and flow conditions Typical data are shown in fig 2. The negative intercept at zero displacement on this Volume 77, number 3



Fig. 2 Logarithm of the ratio of the HO_2 signal with Br_2 discharge off and on versus distance of Br infect from sampling orifice

plot undoubtedly results from poor mixing at the open-ended bromine inlet and is accentuated in this run by the least-squares plot giving equal weight to the point at 40 cm (where the HO₂ signal is very weak). The data points in individual runs, as well as the rate constants from different runs showed considerable scatter, primarily as a result of the low signal-to-noise ratio of the HO₂ signals. The result of nine measure ments of the rate constant is $k = (2.2 \pm 1.1) \times 10^{-1.3}$ cm³ molecule⁻¹ s⁻¹ for the reaction

$$Br + HO_2 \rightarrow HBr + O_2 \tag{6}$$

where the error limits are given as the standard deviation of the measurements. Corrections for radial and axial diffusion are not important at typical conditions employed in these experiments $v \approx 700$ cm/s and $P_{\rm T} \approx 0.5$ Torr. Within the considerable scatter, no correlation of k_6 with [Br] could be observed

In studying the Br + H_2O_2 reaction, the open ended central inlet is replaced by an 8 mm od pyrex tube, terminating in a flattened bulb with six radially directed orifices to facilitate mixing H_2O_2 is added through this central inlet, and bromine atoms are generated by a discharge on a pyrex section of the flow tube Reaction is indicated by changes in the concentration of H_2O_2 (monitored at m/e = 34) when the bromine atom discharge is initiated With the H_2O_2 inlet withdrawn its maximum distance from the sampling orifice (40 cm) a 3% diminution in the H_2O_2 signal could be observed by throttling the flow to 150 cm/s Rate constants of 0.7 and 1.3 × 10⁻¹⁵ cm³ molecule⁻¹ s^{-1} were measured as $(t[Br])^{-1} \ln ([H_2O_2]_{off}/[H_2O_2]_{on})$ Systematic kinetic studies were not possible, due to the very small percentage reaction observed In their absence, we can only conclude that double the average value of these measurements, 20×10^{-15} cm³ molecule⁻¹ s⁻¹, can be considered an upper limit to the rate constant of this reaction,

$$B_1 + H_2O_2 \rightarrow HBr + HO_2 \tag{7}$$

A very similar upper limit has recently been placed on this rate constant by Leu [11]

3 Discussion

Kinetic data for the reactions of Cl and Br with H_2O_2 and HO_2 are listed in table 1 Assuming that the difference in the rate constant of the Cl and Br reactions is entirely due to an activation energy difference, it is found that, in reaction with HO_2 , Br has a 3 3 kcal/mole higher activation energy than Cl, and in reaction with H_2O_2 the difference is greater than 3 6 kcal/mole. These differences correspond to 0.21 and >0 22 of the 16 kcal/mole difference in the exothermicities of the Cl and Br reactions in each case. Semenov has shown that data for a wide variety of exothermic radical-molecule abstraction reactions can be fit by [5].

$$E_{\rm a} = 11.5 + 0.25 \Delta H \,(\text{kcal/mole})$$
 (8)

This relation predicts that differences in E_a are -0.25 times differences in evothermicities A similar reaction between changes of E_a and ΔH approximates the kinetic data for evothermic chlorine and fluorine reactions plotted by Fettis and Knox [15] While quantitative predictions of the above formula should be viewed with considerable caution, it does represent one reasonable basis for *comparing* the kinetics of *chemically similar* reactions of HO₂ and H₂O₂ with Br are much slower than their reactions with Cl is not surprising

Besides H_2O_2 and HO_2 , the only stratospheric component of appreciable concentration with a sufficiently weak bond to hydrogen to react exothermically with Br is formaldehyde. Although stratospheric concentrations of CH_2O have not yet been measured, a few tenths of a part per billion do not seem unrea-

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HR	X = Cl	X = Br	$E_{\mathfrak{g}}(Br) - E_{\mathfrak{g}}(Cl)$ (kcal)	
H ₂ O ₂	$\begin{array}{c} 4 \\ 6 \\ 2 \\ \times 10^{-13} \\ 13 \\ 13 \end{array}$	$<1.5 \times 10^{-15}$ [10] $<2 \times 10^{-15}$ a)	>3 6	
	$av 56 \times 10^{-13}$			
HO ₂	$\begin{array}{cccc} 3 & \times 10^{-11} & [13] \\ 4 & \times 10^{-11} & [14] \\ 6 & 8 \times 10^{-11} & [11] \end{array}$	2×10^{-13} J	331)	
	$av = 4.6 \times 10^{-11}$			

Table 1 Rates constants (cm³ molecule⁻¹ s⁻¹) for X + HR reactions at 298 \pm 3 K

a) This work

sonable as an intermediate in the destruction of CH₄ [15] The reaction of Cl with CH₂O has been found to be very fast ($k = 7.5 \times 10^{-11}$ cm⁻³ molecule⁻¹ s⁻¹) [16] However, it seems likely that the analogous reaction with Br would be considerably slower, as we have observed for the H₂O₂ and HO₂ reactions Considering the rapid rate ($k \approx 10^{-11}$ cm³ molecule⁻¹ s⁻¹) recently measured [16] for the reaction

$$OH + HBr \rightarrow H_2O + Br, \tag{9}$$

It secans that HBr provides a negligible reservoir for stratospheric bromine Since a large fraction of stratospheric chlorine is in the form of catalytically inactive HCl, in this respect, bromine has the potential of being much more destructive than chlorine of the stratospheric ozone layer. A recent computer model of the bromine chemistry of the lower stratosphere [6] has indicated that on a per-atom basis bromine is many times more destructive of ozone than is chlorine. This model calculates that 10-30% of non-organic bromine exists as catalytically inactive HBr in the lower stratosphere If HBr is taken as a negligible bromine reservoir, as indicated by our results, ozone destruction by bromine would be $\approx 20\%$ higher than indicated by these calculations

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References

- [1] R T Watson CIAP Monograph 1 The Narural Stratosphere of 1974, DOT-TST-75-51, Sept 1951
- [2] S C Wolsy, M B McElroy and Y L Yung, Geophys Res Letters 2 (1975) 215
- [3] R T Watson, S P Sander and Y L Yung J Phys Chem 83 (1979) 2936
- [4] M G Evans and M Polanyi Trans Faraday Soc 34 (1938) 11
- [5] N N Semenov, Some problems in chemical kinetics and reactivity, Vol 1 (Princeton Univ Press, Princeton 1958)
- [6] Y L Yung, J P Pinto, R T Watson and S P Sander, J Atmos Sci 37 (1980) 339
- [7] G A Takacs and G D Glass, J Phys Chem 77 (1973) 1060
- [8] M Kaufman and C E Kolb, Chem Instr 3 (1971) 175
- [9] M Kaufman, Pure Appl Chem 48 (1976) 155
- [10] L W Strattan and M Kaufman, J Chem Phys 66 (1977) 4963
- [11] M-T Leu, Chem Phys Letters 69 (1980) 37
- [12] G Poulet, G LeBras and J Combourieu, J Chem Phys 69 (1978) 767
- [13] M-T Leu and W B DeMore, Chem Phys Letters 41 (1976) 121
- [14] J P. Burrows, D.I. Chif, G.W. Harris, B A Thrush and J P.T Wilkinson, WMO Publ 511 (1978) (Paper WMO Symp Geophys Aspects Consequences Changes Compos Strats) pp 25-27
- [15] G C. Fettis and J H Knox, in Progress in reaction kinetics, Vol 2, ed G Porter (1964)
- [16] J V Michael, D F Nava, W A Payne and L.J Stief, J Chem Phys 70 (1979) 1147.