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On the mechanism of the BrO + HBr reaction

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Abstract

The reaction of the bromine oxide radical, BrO, with HBr has been examined with coupled-cluster methods. The HO + HCl reaction is also examined and is used to calibrate the results for the BrO + HBr reaction. The heat of reaction and activation energy barrier for BrO + HBr are calculated to be -9.3 ± 4 and 3.6 kcal mol⁻¹, respectively. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Ozone depletion has been observed in the boundary layer troposphere in the Arctic region [1-3]. During the ozone depletion episodes, mixing ratios of alkanes, alkenes, and alkynes have been found to decrease [4], while formaldehyde increases [5]. Jobson et al. [4] showed that bromine atoms, rather than chlorine atoms, were responsible for most of the ozone destruction. Studies by Hausmann and Platt [6] showed the presence of BrO radicals in the lower Arctic troposphere. These measurements showed that BrO concentrations in the boundary layer were about two orders of magnitude higher than that found in the stratosphere. It has been suggested that the bulk of the ozone loss is most likely caused by BrO_y catalyzed reactions. Modeling studies of Sander et al. [7] show that the BrO self-reaction is a major contributing pathway to the depletion of ozone in the

boundary layer troposphere by the following mechanism,

$$BrO + BrO \rightarrow 2Br + O_2, \qquad (1)$$

$$Br + O_3 \to BrO + O_2. \tag{2}$$

These studies also suggest that the HBr and HOBr mixing ratios are smaller than that of BrO. It has been suggested that most of the HBr produced in the gas phase is scavenged by aerosol particles, and the heterogeneous reaction of HOBr with HBr results in reactive bromine, which reenters into the ozone destruction cycle. The reaction of BrO radicals with HBr to form HOBr allows active bromine (Br atoms and BrO radicals) to form in the gas phase,

$$BrO + HBr \to HOBr + Br.$$
(3)

$$HOBr + h\nu \to OH + Br, \qquad (4)$$

$$Br + O_3 \to BrO + O_2. \tag{5}$$

There has been one previous study of this reaction by Turnipseed et al. [8]. These authors showed that the rate for BrO + HBr reaction has an upper limit of 6.3×10^{-15} cm³ molecule⁻¹ s⁻¹ at 298 K, suggest-

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ing that the reaction is slow. No other experimental studies have been reported for the BrO + HBr reaction. Moreover, no computational studies have been reported for this reaction. The importance of HBr as a sink for bromine in the atmosphere depends critically on the processes that form and destroy HBr. In order to gain some insight into the kinetics of the BrO + HBr reaction, we examine the energetics of this reaction using ab initio molecular orbital theory. We also show the experimental evidence of HOBr formation as a product of BrO reaction with HBr.

2. Computational methodology

All calculations were performed using the GAUSS-IAN 94 program [9]. Geometry optimizations were carried out for all structures using Schlegel's method [10] to better than 0.001 Å for bond lengths and 0.01° for angles, with a self-consistent field convergence of at least 10^{-9} on the density matrix. The residual rms force is $< 10^{-4}$ a.u. Initial searches for the transition state were performed at the B3LYP/6-31G(d, p) level of theory [11,12]. Once the transition state was found, vibrational frequencies were calculated analytically to verify if the transition state was a first-order saddle point. The geometries and second derivatives from the B3LYP/6-31G(d, p) searches were then used in optimizations with the second-order Møller-Plesset perturbation theory (MP2) [13] and with the coupled-cluster method, which included single and double excitations (CCSD) [14-17]. With the MP2 optimizations, Schlegel's analytical gradients method was used. The eigenvalue following method was used to locate the transition state structure, as well as the minimum energy structures with the CCSD method. To refine the energies, singlepoint calculations were performed with the coupledcluster method, which included single and double excitations with perturbative corrections for triple excitations [CCSD(T)], using a range of basis sets which are enlarged by the inclusion of additional sets of d-polarization and a set of f-polarization functions on the bromine and oxygen. The geometry optimized at the CCSD/6-31G(d, p) level of theory was used in the single-point energy calculations. Frequencies and zero-point energy for the species involved in Reaction (1) were evaluated at the B3LYP/631G(d, p) level of theory. The spin contamination before and after annihilation for radical species, and the transition state involved in the BrO + HBr reaction were examined. Before annihilation, $\langle s^2 \rangle$ ranged from 0.787–0.778, and after annihilation, $\langle s^2 \rangle$ was 0.751. This suggested that the wavefunction was not strongly contaminated by states of higher multiplicity.

3. Results and discussion

3.1. Mass spectroscopic observation of the BrO + HBr reaction

A discharge flow combined with mass spectrometer (DF/MS) technique has been employed to briefly study Reaction (3). The detail of the DF/MS setup has been described previously [18]. Fig. 1 shows the mass spectrum for the BrO + HBr system, in which the profile in solid line shows 1.4×10^{13} molecule cm⁻³ of BrO produced by reacting Br₂ with atomic oxygen in the absence of HBr.

$$Br_2 + O \rightarrow BrO + Br$$
. (6)

The atomic oxygen was produced by microwave discharge of O₂. The spectrum reveals two peaks at m/e = 95/97, corresponding to ⁷⁹BrO and ⁸¹BrO isotopes, respectively. The peaks at m/e = 79/81 are the atomic bromine due to both Reaction (5) and fragmentation of Br₂. The profile in the dotted line was taken after addition of 1.4×10^{13} molecule cm⁻³



Fig. 1. Mass spectrum for the BrO+HBr chemical system.

of HBr into the reactor. It can be seen that two new peaks appeared at m/e = 96/98, assigned to be HOBr, when the HBr was added to the reactor containing BrO. The decrease of the BrO peaks and the appearance of HOBr upon addition of HBr suggest that the hydrogen abstraction of HBr by BrO is one reaction pathway for the interaction between BrO and HBr. The increase of the m/e = 79/81 in the dotted profile may be due to the additional atomic bromine produced by Reaction (3) and by the fragmentation of HBr.

3.2. Geometries and vibrational frequencies for the BrO + HBr reaction

Table 1 lists the geometries for the reactants, transition state, and products of the BrO + HBr reaction. Table 2 lists the CCSD/6-31G(d, p) vibrational frequencies and zero-point energies for the BrO + HBr reaction. The transition state for the BrO + HBr reaction is shown in Fig. 2. In the approach of the BrO into the entrance channel, the H–Br bond length begins to elongate. The transition state involves mainly three atoms in the abstraction process. They are the oxygen atom from the BrO, and the hydrogen atom and the Br atom from HBr. In the transition state, the H–Br bond elongates by 13% of its equilibrium value. The O–H bond length in HOBr is only 29% of that of the transition state. The attacking

Table 1

Species	Coordinate	CCSD	Expt.	
BrO	r(BrO)	1.777	1.728	
HBr	r(HBr)	1.410	1.448	
HOBr	r(HO)	0.968		
	r(BrO)	1.869		
	θ (HOBr)	102.1		
[BrO+HBr] [‡]	r(BrO)	1.806		
	r(OH)	1.246		
	r(HBr)	1.588		
	θ (HOBr)	109.6		
	θ (OHBr)	152.4		
	τ (BrOHBr)	81.7		

^a The CCSD structures are obtained with the 6-31G(d, p) basis set. Bond distances are in units of Å, and bond angles are in degrees. Table 2

Harmonic vibrational frequencies for species involved in the ${\rm BrO} + {\rm HBr}$ reaction

Species	Frequencies $(cm^{-1})^a$	ZPE (kcal mol ⁻¹)
BrO	705	1.0
HBr	2622	3.7
HOBr	3776, 1190, 636	8.0
[BrO+HBr] [‡]	1003, 842, 668, 343, 68, 922i	4.2

^aCalculated at the B3LYP/6-31G(d, p) level of theory.

oxygen atom and the hydrogen and bromine atoms are predicted to be not co-linear, as is usually the case for most hydrogen abstraction reactions by halogen atoms [19,20]. For BrO + HBr reaction, the optimized OHBr angle in transition state is predicted to be 152.4° , although optimization was started with a linear configuration. The transition state was started in this position due to results presented by Clary et al. [21]. Note that the resultant transition state structure is found to be non-planar with a BrOHBr dihedral angle of 81.7° . From the geometric changes in the forming OH and breaking HBr bonds, the saddle point for the BrO + HBr appears to be more reactant-like. This is consistent with Hammond's rule [22] for exothermic systems.

The vibrational frequencies, the reactants, and product in Reaction (3) are all real, and the transition state for the BrO + HBr reactions shows one imaginary frequency of 922i cm⁻¹. The transition state vibrational reactors show that the main molecular motions are the H–Br and OH stretching motions, as indicated in Fig. 2.

3.3. Energetics of the BrO + HBr reaction

In order to obtain an estimate of the reliability of the prediction for the energetics for the BrO + HBr



Fig. 2. Transition state structures for the BrO+HBr reaction.

reaction, we investigated the HO + HCl reaction, for which there have been considerable experimental and theoretical studies [21,23–30]. The most extensive experimental studies of the HO + HCl reaction have been those of Smith and Zellner [24] who covered the temperature range between 220 and 480 K, Ravishankara and co-workers [25] who measured rate constants from 240 to 1055 K, and the recent low-temperature measurements of Sharkey and Smith [30] from 138 to 298 K. The Jet Propulsion Laboratory (JPL) compilation [31] in evaluating all measurements of the HO + HCl reaction recommends that the best activation barrier is 0.695 ± 0.2 kcal mol⁻¹.

Clarv and co-workers [21] obtained an activation barrier height of 24.7 kcal mol⁻¹ at the UHF/6-311 + + G(d, p) level of theory. The authors acknowledged that the calculated barrier height is much too large at this level of theory. When electron correlation is included at the MP2 level, the barrier is predicted as 7.2 kcal mol^{-1} . The barrier height for the HO + HCl reaction calculated with the CCSD/6-31G(d, p) level of theory is 6.7 kcal mol⁻¹. With the CCSD(T)/6-31G(d, p), the barrier is lowered by $1.8 \text{ kcal mol}^{-1}$. These computational results suggest that the high-level calculations are necessary to predict the activation energy barrier of hydrogen abstraction processes, but the predicted E_a in previous studies is still too high. Extending the size of the basis set improves the results, as shown in Table 3. At the CCSD(T)/6-311 + + G(2df, 2p)//CCSD/6-31G(d, p) level of theory, the barrier is estimated as 3.1 kcal mol⁻¹. This barrier is corrected for zero-point energy, but not tunneling corrections. When tunneling corrections are included in the barrier using the Wigner correction [32] employing the imaginary frequency of 2003i from the UMP2/6-31G(d, p) frequency calculation, the resultant barrier for the HO + HCl reaction is 2.4 kcal mol⁻¹. This suggests that the calculations overestimate the experimental barrier by 1.7 kcal mol⁻¹.

The experimental heat of reaction $(\Delta H_{r,0}^{\circ})$ is well established as -16.0 ± 0.01 kcal mol⁻¹. At the CCSD(T)/6-311G(2df, 2p)//CCSD/6-31G(d, p) level of theory, the predicted heat of reactions is -13.9 kcal mol⁻¹, as shown in Table 3, which is overestimated by 2.1 kcal mol⁻¹ from the experimental heat of reaction. At the CCSD(T)/6-311 + + G(2df, 2p)//CCSD/6-31G(d, p) level of theory, the calculations are within 0.4 kcal mol⁻¹ of the experimental heat of reaction. This suggests that the energetics for the BrO + HBr reaction can be reasonably predicted at the highest level of theory of the present study, keeping in mind that the barriers are probably overestimated by 2 kcal mol⁻¹.

The experimental heats of formation at 0 K are 30.2 ± 1 , -10.93 ± 1 , 28.2 ± 0.0 , and -6.8 ± 1 kcal mol⁻¹ for BrO [33], HOBr [34], Br [33], and HBr [33], respectively. This leads to an experimental heat of reaction of -6.1 ± 1 kcal mol⁻¹. The calcu-

Table 3 Total and relative energies for the HO + HCl reaction

Level of theory	Total energies (hartree)				Relative energies ^a (kcal mol ⁻¹)		
	Cl	НО	HCl	H ₂ O	$[HO + HCl]^{\ddagger}$	$\Delta H_{ m r,0}^{ m o}$	barrier height
CCSD/6-31G(d, p)	-459.56897	-75.54673	-460.22194	-76.22877	- 535.75791	-14.3	6.7
CCSD(T)/	-459.57048	-75.54845	-460.22457	-76.23158	-535.76524	-14.2	4.9
6-31G(d, p)							
CCSD(T)/	-459.60325	-75.58917	-460.26331	-76.27611	-535.84541	-13.0	4.4
6-311G(d, p)							
CCSD(T)/	-459.62456	-75.60811	-460.28753	-76.29891	-535.89073	-13.6	2.5
6-311G(2d, 2p)							
CCSD(T)/	-459.65734	-75.62701	-460.32131	- 76.31934	- 535.94427	-13.9	2.5
6-311G(2df, 2p)							
CCSD(T)/6-311 + +	-459.65873	-75.63348	-460.32249	-76.32826	-535.95102	-15.6	3.1
G(2df, 2p)							
Expt.						-16.0 ± 2	0.695 ± 0.2

^aRelative energies are corrected for zero-point energy calculated at the MP2/6-31G(d, p) level of theory.

8					
Level of theory	Br	BrO	HBr	HOBr	$[BrO + HBr]^{\ddagger}$
CCSD/6-31G(d, p)	- 2569.96967	-2644.92974	-2570.60728	-2645.58623	- 5215.52223
CCSD(T)/6-31G(d, p)	-2569.97056	-2644.93731	-2570.60916	- 2645.59393	-5215.53460
CCSD(T)/6-311G(d, p)	-2572.46866	-2647.46533	-2573.10788	-2648.12629	-5220.56125
CCSD(T)/6-311G(2d, 2p)	-2572.47042	-2647.49246	-2573.11326	-2648.15451	-5220.59439
CCSD(T)/6-311G(2df, 2p)	-2572.50377	-2647.54997	-2573.14621	-2648.21239	-5220.68604
CCSD(T)/6-311 + + G(2df, 2p)	-2572.50408	-2647.55596	-2573.14667	-2648.21854	-5220.70767

Table 4 Total energies^a for the BrO + HBr reaction

^aTotal energies are in units of hartree.

lated total energies for the reactants and products and the relative energetics for Reaction (3) at various levels of theory are presented in Tables 4 and 5, respectively. At the CCSD and CCSD(T) levels, the heat of reaction for the BrO + HBr reaction is predicted to be exothermic by 8-10 kcal mol⁻¹, as shown in Table 5. At the CCSD(T)/6-311G(2df, 2p)//CCSD/6-31G(d, p) level of theory, the heat of reaction is predicted to be -9.3 kcal mol⁻¹. There is a 3.2 kcal mol⁻¹ difference between the calculation and experimental estimate for the BrO + HBr reaction.

The calculated barrier height for the abstraction of hydrogen from HBr by BrO ranges from 8.8 to 6.4 kcal mol⁻¹, depending on the level of theory and basis set, as seen in Table 5. At the CCSD(T)/6-311 + + G(2df, 2p)//CCSD/6-31G(d, p) level of theory, the activation barrier for the BrO + HBr reaction is estimated as 6.8 kcal mol⁻¹. Adding tunneling corrections, and from our examination of the HO + HCl reaction, we find that the barrier calculated at this high level is probably overestimated by an additional 1.7 kcal mol⁻¹. If we include these

Table 5 Heat of reaction and barrier height for the BrO+HBr reaction

Level of theory	$BrO + HBr \rightarrow Br + HOBr$			
	$\overline{\Delta H^{\mathrm{o}}_{\mathrm{r},0}{}^{\mathrm{a}}}$	barrier height ^a		
CCSD/6-31G(d, p)	-8.6	8.8		
CCSD(T)/6-31G(d, p)	-8.1	6.9		
CCSD(T)/6-311G(d, p)	-10.4	7.0		
CCSD(T)/6-311G(2d, 2p)	-8.8	7.1		
CCSD(T)/6-311G(2df, 2p)	-9.3	6.4		
CCSD(T)/6-311 + + G(2df, 2p)	-9.3	6.8		
Expt.	-6.1 ± 1			

^a The heat of reaction and barrier are corrected only for zero-point energy and are reported in units of kcal mol⁻¹.

contributions, a reasonable estimate of the barrier is $3.6 \text{ kcal mol}^{-1}$.

3.4. Estimation of the reaction rate for the BrO + HBr reaction

To estimate the rate constant for the BrO + HBr reaction, transition state theory (TST) is used. The basic postulate of transition state theory is that the rate of transformation of the reactants to products is given solely by the passage in the forward direction of reactants through the transition state, then onto products. Calculation of the partition functions for the transition state and reactants coupled with the activation energy then yields a thermal rate constant. This is given by the following equation:

$$k(T) = \left(\frac{k_{\rm B}T}{h}\right) \left(\frac{Q^{\ddagger}}{Q_{\rm A}Q_{\rm B}}\right) \exp(-E_0/RT).$$
(7)

In order to evaluate the reasonableness of the A-factor calculated solely from ab initio data, a calibration calculation was first carried out on the HO + HCl reaction. From the geometries and vibrational frequencies for the reactants (HO and HCl) and the abstraction transition state, the partition functions are calculated. Using the first two terms in Eq. (7), the A-factor can be calculated. The recommended A-factor from the JPL compilation [31] for the HO + HClreaction is 3.2×10^{-12} cm³ molecule⁻¹ s⁻¹. Using the ab initio data and transition state theory, our estimated A-factor is 2.6×10^{-12} cm³ molecule⁻¹ s^{-1} . There is a difference of 23.1% between the experimental and the calculated value. The difference between the two values is attributed to the uncertainty in the calculated rotational constants and vibrational frequencies in the calculations. From our examination of the A-factor from the HO+HCl

reaction, we find that it may be necessary to scale the A-factor calculated from the ab initio results. This further suggests that in order to estimate the A-factor for the BrO + HBr reaction, it is necessary to scale the A-factor. In the BrO + HBr, we use the scale factor derived from the HO + HCl reaction in conjunction with the A-factor derived from transition state theory using the ab initio parameters. The estimated kinetic rate constant for the BrO + HBr reaction is 2.1×10^{-14} cm³ molecule⁻¹ s⁻¹ at 298 K. This value represents an average of rates over the uncertainty range of the activation energy barrier for the BrO + HBr reaction. The results suggest that the BrO + HBr reaction is slow, and is roughly of a magnitude that is similar to the upper limit result of Turnipseed et al. [8].

4. Summary

The reaction products and relative energetics for the reaction of BrO + HBr have been examined. The reaction of BrO with HBr was found to produce HOBr. In general, increasing the basis set and improving the level of theory lowers the calculated activation barrier. This trend shows that it is necessary to do these kinds of calculations with large basis sets and at high levels of theory. The heat of formation is calculated at CCSD(T)/6-311 + + G(2df, 2p)//CCSD/6-31G(d, p) level of theory to be -9.3 ± 4 kcal mol⁻¹. The activation barrier is estimated to be 3.6 kcal mol⁻¹ at the same level of theory.

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