J. Phys. Chem. A **1998,** *102,* 1083−1089

Reversible Photoinitiated Isomerization Reaction of BrOBr to BrBrO: A Combined Matrix Isolation and ab Initio Study

Jennifer Kölm, Otto Schrems, and Peter Beichert*

Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12,
D-27570 Bremerhaven, Germany

Received: September 22, 1997; In Final Form: November 19, 1997

The reversible photoinitiated isomerization reaction of BrOBr to BrBrO was measured in solid argon matrixes and calculated by multiconfigurational quasidegenerate perturbation theory (MCQDPT). The calculated vertical excitation energies are in good agreement with the experimentally observed excitation wavelengths. While the isomerization from BrOBr to BrBrO appears to be quantitative, some product loss is observed during the back reaction. The calculated excitation energies and oscillator strengths for transitions from the ground to excited states offer a detailed explanation of this behavior.

Introduction

The halogen oxides show strong variations in structural parameters and other physical as well as chemical properties. Many chlorine oxides are known and have been quite well characterized recently. In comparison with the chlorine oxides, the bromine oxides are much less stable, and only a few of them have been investigated.[1] A number of bromine-containing compounds, of either biogenic or anthropogenic origin (e.g., methyl bromide), released at the earth's surface have been linked to ozone destruction[2] in various altitude regions of the earth's atmosphere. Examples are the ozone hole in the lower stratosphere of the Antarctic[1] and the ozone depletion events in the lower Arctic troposphere in spring.[3] The catalytic cycle is similar to that of chlorine. Although bromine is a minor constituent of the atmosphere (troposphere and stratosphere), it is known to have a stronger ozone depletion potential than chlorine.[4] Consequently, the interest in characterizing atmospheric bromine species spectroscopically as well as by ab initio calculations has been stimulated in the last few years.

The low thermal stability and the difficulty of obtaining the bromine oxides in a pure state are the main reasons why their thermochemistry and IR and UV spectra are not yet well characterized. Of the known oxides, the most stable ones are dibromine monoxide, presumably with a bent BrOBr structure, and bromine dioxide, whose structure is so far unknown. Most frequently, Br_2O is used as a precursor for the synthesis of hypobromous acid,[5,6] HOBr, an important bromine species in the atmosphere.[7,8]

$$Br_2O + H_2O \rightarrow 2\,HOBr \tag{1}$$

$$HOBr + HCl \rightarrow BrCl + H_2O \tag{2}$$

$$HOBr + h\nu \rightarrow OH + Br \tag{3}$$

The first hints in the literature pointing to dibromine monoxide produced by the heterogeneous reaction of bromine and mercury oxide were given by Zintl and Rienäcker in 1930.[9] Seven years later Schwarz and Schmeisser[10] synthesized a yellow solid of the composition BrO_2 by passing a gaseous mixture of bromine and oxygen through a dc-discharge tube. These authors claimed the structure of this substance to be the symmetric bromine dioxide (OBrO). In their experiments the reaction products were trapped directly in the discharge tube with liquid air. They found that the yellow compound decomposes near 0 °C into BrOBr. Also Campbell et al.[11] and Levason et al.[12] prepared BrOBr by this two-step process. In these experiments BrOBr was characterized by infrared spectroscopy[11,12] and with EXAFS[12] from which the structure of BrOBr was obtained. Another method for synthesizing BrOBr was reported by Schmeisser and Jörger.[13] They ozonolyzed bromine in a cooled CCl_3F solution and obtained OBrO, which subsequently decomposed to BrOBr and oxygen.

The UV−visible absorption cross sections of gaseous dibromine monoxide have been reported by Rattigan et al.[6] and Orlando and Burkholder.[14] The rotational spectra[15] and the photoionization efficiency spectrum[16] of dibromine monoxide were measured as well.

Matrix isolation spectroscopy is a powerful technique for examining unstable species and allows studying photochemical reactions separately from thermochemical ones. Tevault et al.[17] used this advantage to produce both dibromine monoxides directly in a rare gas matrix. BrBrO was observed among several other bromine oxides after photolyzing an $Ar/Br_2/O_3$ matrix with light at 632.8 nm. During extensive exposure of the matrix to the long wavelength radiation of a Nernst glower, a new band appeared at 526.1 cm^{-1} which was assigned to the symmetric dibromine monoxide (BrOBr).

In this contribution we report the results of our studies of the reversible photoisomerization of BrOBr to BrBrO and vice versa. The symmetric dibromine monoxide (BrOBr) was synthesized and purified prior to deposition in solid argon. This allowed us to study the photoisomerization free from any side reactions due to the presence of ozone, oxygen atoms, molecular bromine, or other bromine oxides. We were able to follow the photoisomerization from BrOBr to BrBrO as well as the back reaction.

$$BrOBr + h\nu \rightarrow BrBrO \tag{4}$$

$$BrBrO + h\nu \rightarrow BrOBr \tag{5}$$

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* Author to whom correspondence should be addressed.

S1089-5639(97)03082-X CCC: $15.00

Bromine-containing species have been a challenge for computational chemists because the large number of electrons in bromine make precise calculations difficult and expensive. In 1992, Novak[18] calculated the structure of BrOBr using Hartree−Fock theory. The accuracy of these calculations is not very high since Hartree−Fock calculations neglect the electron correlation—which is quite important for bromine-containing species—completely. With CCSD(T) calculations and a TZ(2P) basis set, Lee[19] was able to calculate the ground-state geometries and properties of BrOBr and BrBrO very precisely. These calculations were compared to those achieved with the DFT (density functional theory) by Chaquin et al.[20] The computational cost of the DFT calculations are much lower than for classical correlated ab initio calculations, and the geometries get reproduced quite well. However, the calculated energies of the compounds showed some discrepancies.

Our approach was to calculate the isomerization reaction of the two Br_2O species. For this purpose we had to optimize the two ground-state geometries as well as the geometry of the transition state at the MP2 level. In addition we calculated the harmonic vibrational frequencies at this level. From the transition state we were able to follow the intrinsic reaction coordinate (IRC) in mass-weighted Cartesian coordinates in both directions to BrOBr and BrBrO. To investigate the influence of nondynamical correlation effects, we optimized the geometries of ground and transition states in addition at multiconfigurational SCF level. This procedure is also known as complete active space self-consistent field (CASSCF) calculation where we choose the complete valence shell as the active space. This leads to minimal longer bonds. Since the isomerization reaction is photolytically induced and not thermally initiated, we also calculated the vertical excitation energies. For this purpose we applied the multiconfigurational quasidegenerated perturbation theory second-order (MCQDPT2)[21] to the MCSCF reference functions and calculated the excited singlet and triplet states at the ground-state equilibrium geometry. To access the strength of the transition, we calculated the radiative transition moments for the transitions from the ground states to higher singlet states.

Experimental Section

Br_2O was prepared via the heterogeneous reaction of bromine vapor with solid mercury oxide,[14,17] in analogy to the Cl_2/Cl_2O system:

$$2Br_2 + HgO(s) \rightarrow HgBr_2(s) + BrOBr \qquad (6)$$

Approximately 50 g of HgO powder (Riedel de Haën, p.a.) was placed on the base of a cylindrical 2 L glass bulb equipped with inlet and outlet valves. The glass bulb was evacuated to a pressure of about 4 hPa. Bromine (Merck, >99%) was degassed and dried by passing the bromine stream through a trap filled with phosphorus pentoxide (Merck, Sicapent). The evacuated glass bulb was then filled with bromine up to a pressure of 130 hPa. After 5 min of equilibration of the reactants and products, the gases were pumped through a trap cooled with liquid nitrogen. This procedure was repeated several times to obtain a sufficient quantity of BrOBr in the cold trap. The temperature of the trap was then raised to about 230 K, and Br_2 was removed by pumping. Toward the end of the pumping procedure, after about 4 h, an olive green powder remained in the trap.

For the deposition in the matrix, the trap with the dibromine monoxide was attached directly in front of a sample chamber equipped with a gold mirror and cooled by a Leybold RW2 cryogenerator. To reach a sufficient vapor pressure of BrOBr, the trap was kept at 223 K during the deposition. A flow of 0.1 $cm^3\ s^{-1}$ of argon (Messer Griesheim, 4.8) was passed over the BrOBr to dilute and to deposit BrOBr onto the gold-plated mirror whose temperature was kept at 17 K by a Lake Shore DRC-93C temperature controller.

The IR spectra were recorded in reflection mode with a FTIR spectrometer (Bruker IFS66v) between 400 and 4000 cm^{-1} and at a resolution of 0.5 cm^{-1}. We used an 800 W Xe/Hg-deep UV lamp (Ushio) combined with a 1/8 m monochromator (ORIEL) to irradiate the matrix with UV light.

Computational Methods

Equilibrium geometries of BrOBr and BrBrO and the transition-state geometry between them have been determined at nonrelativistic MP2 level. As basis sets we used the 6-31G (3D1F)[22] set for oxygen, and a 9s,6p,2d contraction of a 14s,11p,5d primitive set with an additional set of d and f polarization functions for bromine as given by Binning and Curtiss.[23] In the following we refer to this basis as full basis. The use of valence-only basis sets with the corresponding effective core potentials (ECPs) allows one to determine the molecular properties at considerably lower computational cost. We compared the SBK(3D) set of Stevens, Basch, and Krauss[24] and the HW(3D) set of Hay and Wadt[25] with the above-mentioned full basis set. The optimized geometries at MP2 level with the SBK(3D) basis set are comparable to the one with the full basis set, while the HW(3D) set led to unrealistic long bonds in the case of BrOBr and therefore was not applied further. ECP basis is used in the following text for the SBK(3D) basis. Relativistic corrections for compounds containing bromine are small enough to not be a problem in determining molecular parameters in ab initio calculations.[26] The harmonic frequencies were determined by the numerical calculation of the second-derivative energy tensor at the same theoretical level. While restricted Hartree−Fock (RHF) calculations neglect electron correlation completely, the MP2 level recovers about 80% of it. However, since the performance of perturbation theory depends critically on the zeroth-order Hamiltonian, single-reference MP theory fails in dealing with nondynamical correlation (i.e., for bond fragmentation and nearly degenerate states). Perturbation theory gives only good results if the perturbation is small and therefore the perturbation series converges rapidly. This is not the case where the Hartree−Fock approximation is not a good starting point. An accurate determination of the geometries at the RHF-MP2 level can therefore only be expected for the ground-state equilibrium geometries, while the transition state should have a larger error. Since the geometry of the transition state is relatively close to those of the two ground states, the geometry of the transition state calculated at RHF-MP2 level can be used for a first guess, although the accuracy should be expected to be lower. Therefore, starting from the RHF-MP2 equilibrium geometries we optimized all geometries again at CASSCF level (the complete valence shell is used as active space), which includes the state specific nondynamical correlation. The CASSCF wave function consists of 1716 configuration-state functions. The CASSCF level describes qualitatively the whole potential energy surface correctly. The resulting transition-state geometry should be accurate with an error of less than 0.1 Å. However, the energies resulting from the CASSCF calculation do not include the dynamical electron correlation and therefore are not able to determine the energy differences of the different species within

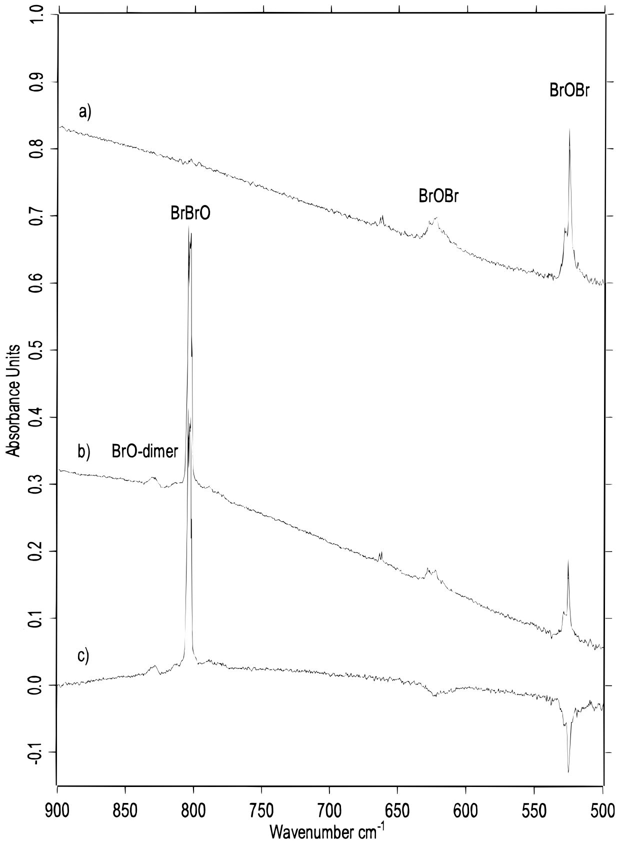

Figure 1. Infrared spectra of BrOBr isolated in solid argon at 17 K (a) after deposition; (b) after irradiation with light of 380 nm; (c) difference spectrum.

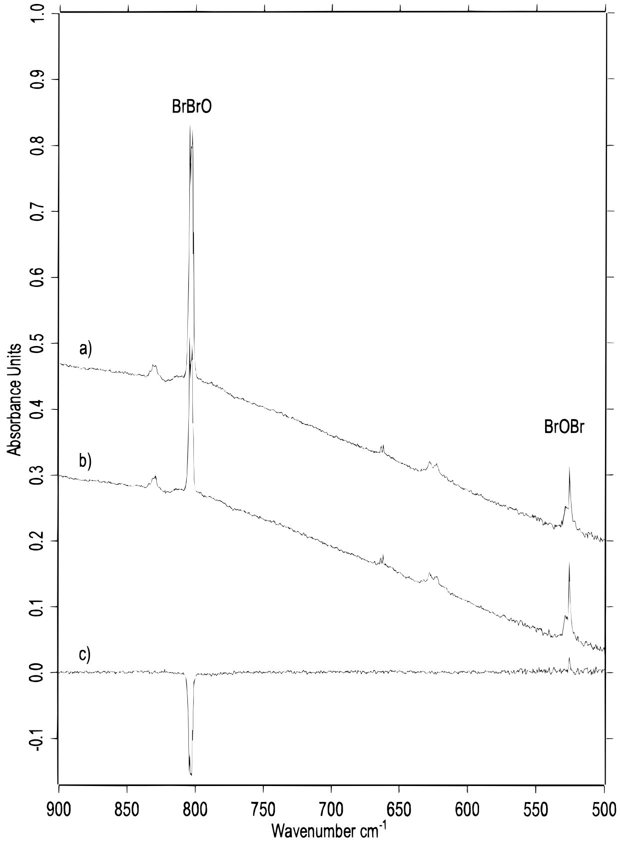

Figure 2. Infrared spectra of BrBrO and BrOBr isolated in solid argon at 17 K (a) before irradiation; (b) after irradiation with light at 330 nm; (c) difference spectrum.

chemical accuracy. To improve this energy, we applied the quasidegenerated perturbation theory developed by Nakano[21] with the MCSCF reference functions at the equilibrium geometry. This multistate perturbation theory is size consistent and yields fairly accurate results compared with traditional highly correlated methods like multireference configuration interaction (MR-CI), while it needs less calculation time and is therefore more efficient, as demonstrated by Nakano[21,27] on a number of examples.

After the equilibrium geometries of BrOBr and BrBrO and the geometry of the transition state were calculated, the calculation of the intrinsic reaction coordinate (IRC) was performed using the SBK valence-only basis set. The IRC is the minimum energy path connecting the reactants to the products via the transition state. Starting from the transition state, the IRC was found by following the steepest descent path in mass-weighted Cartesian coordinates. All calculations were performed using the GAMESS[28] program system.

Results

Matrix Isolation Experiments. After BrOBr was deposited in an argon matrix the symmetric stretching vibration (ν_1) at 525.3 (±0.5) cm^{-1} as well as the asymmetric stretching vibration (ν_2) at 622.2 (±0.5) cm^{-1} (Figure 1a) could be observed. These frequencies are in good agreement with the available literature data.[12,17,29] The matrix-isolated BrOBr can be rapidly photoisomerized to BrBrO with light of the wavelength range between 350 and 400 nm. The intensities of the BrOBr bands decrease and the Br−O stretching vibration band (ν_3) of BrBrO grows at 804.7 (±0.5) cm^{-1} (Figure 1b). In addition to the bands of the Br_2O isomers, there appears a very weak band at 829.9 cm^{-1} which belongs to the BrO dimer. No additional product peaks are detectable in the difference spectrum (Figure 1c). A very slow isomerization could also be observed with light between 400 and 600 nm, although the yield was very low even after an irradiation time of several hours. With light of wavelengths shorter than 340 nm, BrBrO photoisomerizes back to BrOBr (Figure 2). The isomerization procedure can be repeated several times. However, a certain amount of product loss can be observed. This product loss cannot be explained by the formation of the BrO dimer alone since this formation should be limited by the amount of cages with two Br_2O molecules. No additional peaks appear in the spectra during this irradiation procedure, which could explain the product loss.

At a slower rate the isomerization reaction from BrBrO to BrOBr can also be observed with long wave infrared light of the Nernst glower as reported by Tevault et al.[17] This requires typical irradiation overnight in order to see a product change with a significant signal. If the matrix is irradiated with light at 345 ± 10 nm, no photoisomerization seems to occur and the relative intensities of the absorption bands of BrOBr and BrBrO do not change.

Ab Initio Calculations. Table 1 shows the calculated geometry parameters in comparison with available literature data. The bond lengths and bond angle of BrOBr are comparable to the experimental values of Levason et al.[12] and to those calculated by Lee.[19] There are no experimental values for BrBrO available, but our calculations agree quite well with those of Lee. The MP2 bond lengths are generally somewhat shorter than those calculated by Lee, while the CASSCF values are slightly longer. For the transition-state geometry there are no values available in the literature. Regarding the good agreement for BrOBr and BrBrO the results are quite trustworthy. Nevertheless, the accuracy of the values is expected to be lower than that for the ground-state geometries of BrOBr and BrBrO.

TABLE 1: Calculated Geometry Parameters in Comparison with Literature Values (Bond Distances (r) in pm, Angles (α) in deg)

	Levason et al.[12] expt[a]	Lee et al.[19] CCSD(T) TZ2P basis	this work			
			MP2 ECP basis	MP2 full basis	CASSCF ECP basis	CASSCF full basis
BrOBr						
rOBr	185.(1)	186.5	187	186	190	188
rBrBr	307.(2)		309	307	314	311
αBrOBr	112 ± 2	112.9	111.2	112.0	111.6	111.6
BrBrO						
rOBr		169.0	165	164	172	170
rBrBr		251.0	248	245	258	255
αBrBrO		113.1	113.9	112.8	114.3	113.6
TS[b]						
rOBr1			184	183	192	
rOBr2			230	229	230	
rBrBr			246	245	249	
αBrOBr			71.8	72.2	71.7	

[a] Obtained from an EXAFS study at 160 K. [b] TS = transition state.

TABLE 2: Calculated and Experimentally Observed Absorption Frequencies of BrOBr, BrBrO, and the Transition State as Well as Relative Energies to BrOBr[a]

	BrOBr			BrBrO				TS			
	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ΔE (eV)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ΔE (eV)
MP2 ECP basis	517	183	625	231	161	1040	0.85	i1534	291	727	3.60
MP2 full basis	537	191	676	242	170	1056	0.80	i1599	295	754	3.58
CASSCF ECP basis	476	171	559	163	124	711	0.80	i1326	299	543	3.38
CASSCF full basis							0.90				3.20
MCQDPT2 ECP							0.72				2.80
MCQDPT2 full							0.67				2.60
expt (Ar matrix)	525.3		622.2			804.6					
Lee et al.[19] (CCSD(T))	513	180	613	215	153	793	0.70				
Tevault et al.[17] (Ar matrix)	526.1			235.8		804					
Levason et al.[12] (N_2 matrix)	528		626								
Allen et al.[29] (Ar matrix)	526.1		623.4								

[a] Imaginary frequencies of the transition state are indicated by an "i" in front of the number.

The calculated harmonic frequencies of BrOBr at the MP2 level, with the full basis as well as with the ECP basis, agree quite well with the values calculated by Lee[19] and are close to the experimental anharmonic frequencies measured in noble gas matrixes (Table 2). On the other hand, the frequency of the BrO stretching vibration of BrBrO is clearly too high. This is due to the limitations of the MP2 procedure and was observed earlier for the ClO stretching vibration of ClClO.[20] At the CASSCF level the harmonic frequencies are, in general, too low for the vibrations of BrOBr and BrBrO. All calculations show one imaginary frequency for the optimized transition state which proves that it is a real transition state and not only a saddle point in the potential energy surface. The CASSCF frequencies for the transition state are again lower than those calculated at the MP2 level.

The energy difference between BrOBr and BrBrO seems to decrease with the inclusion of electron correlation which should be due to the closer distance of the two heavy bromine atoms. The MCQDPT2 calculations result in similar energy differences like the CCSD(T) calculations of Lee.[19] Even at the MP2 level the energy differences are only about 0.1 eV higher. The discrepancies of the energy difference between the transition state and BrOBr calculated at the MCQDPT2 and MP2 levels are much higher. This is due to the fact that a single Hartree–Fock wave function is not a very good zeroth-order approximation for this transition state. Therefore the MP2 calculations of the transition state have a larger error than those for the ground-state equilibrium geometries. However, in the transition state the bond length between the atoms are already higher, although no bond dissociation is observed.

The calculation of the product, reactant, and transition state of a reaction gives an idea how the reaction can proceed. However, the dependency of the geometrical parameters from the energy cannot be linearly interpolated. For this purpose it is necessary to calculate the IRC. The IRC of the isomerization reaction is shown in Figure 3. Because many points are necessary for the calculation of the IRC, it was only possible to calculate it at the MP2 level with the ECP basis set. The bond angles of BrOBr and, respectively, BrBrO are changing during the whole reaction. The bond distance between the two Br atoms decrease from BrOBr to the transition state, but remain nearly constant from the transition state to BrBrO. On the other hand, one of the BrO bond distances remains constant during the reaction from BrOBr to the transition state, immediately gets shorter afterward, and remains constant again for the rest of the reaction until the equilibrium BrBrO geometry is reached. The other BrO distance only remains constant for a small amount of the reaction path from BrOBr to the transition state and then increases than constantly toward BrBrO.

At the CASSCF and MCQDPT2 levels we calculated not only the ground-state but also the excited-state energies. The results are summarized in Table 3. The differences between the CASSCF and MCQDPT2 results show that the inclusion of the dynamical correlation is quite important. For BrOBr it generally lowers the energy of the excited states relative to that of the ground state, while for BrBrO the energies of the excited states get higher. To obtain an idea about the probability for the radiative transition from the ground to the excited state, we calculated the oscillator strength for these transitions. The transitions from the singlet ground state to the triplet states are

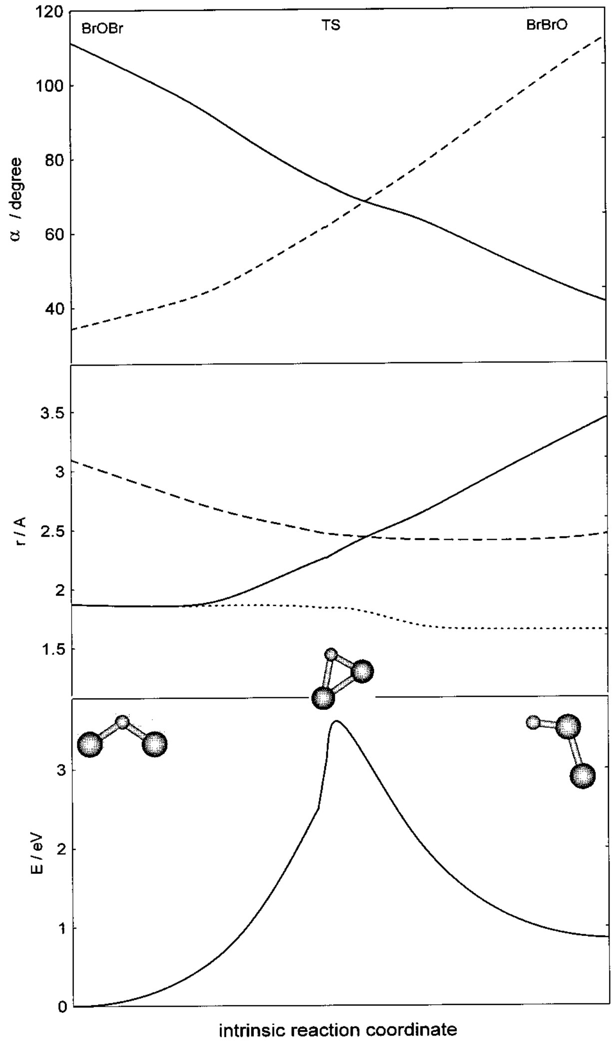

Figure 3. Calculated IRC at the MP2 level with the ECP basis set. Upper part: change in BrOBr angle (solid) and BrBrO (dashed) angle during the reaction. Middle part: change in BrO distances (solid and dotted) and BrBr distance (dashed) during the reaction. Lower part: energy change.

generally spin forbidden and should be zero. However, for molecules which contain heavy atoms, weak intercombinations may occur and the spin selection rule is no longer strictly valid.[30] Therefore we also calculated the transitions to triplet states. The results of the calculation in Table 3 show that these transitions are not important in the photoisomerization reactions. BrOBr belongs to the C_{2v} point group with an A_1 ground-state symmetry. The transition to excited states which also have A_1 symmetry are very weak and those to A_2 symmetry states are symmetry forbidden and therefore also zero. The excited singlet state with the lowest energy is that with the B_2 symmetry. The energy difference to the ground state is 2.16 eV, which corresponds to an excitation wavelength of 575 nm. This energy is not high enough to initiate the direct isomerization reaction via the transition state. The calculated oscillator strength for the transition from the ground state to this excited state is with 8.4×10^{-4}, about 1 order of magnitude lower than for the oscillator strength to the lowest B_1 state. For this stronger transition, light with 399 nm wavelength (3.11 eV) is needed. This energy is high enough to reach the transition state. BrBrO belongs to the point group C_1 and therefore all transitions into higher singlet states are allowed. However, as it can be seen from the oscillator strength in Table 3 the first transitions are very weak. Only the transition which can be initiated with light of a wavelength of 330 nm (3.77 eV) is orders of magnitude stronger.

Discussion

Figure 4 shows a diagram of the photoisomerization of Br_2O. Upon irradiation of isolated BrOBr with light between 400 and 600 nm, the IR absorption bands of BrOBr diminish very slowly, while a new band due to BrBrO appears. The calculations show that there should be a weak absorption at about 575 nm due to the transition to the lowest excited singlet state. However, the corresponding energy of 2.16 eV is not high enough to reach the transition state which is, according to the MCQDPT calculation, 2.60 eV higher than the ground state of BrOBr. The isomerization at these wavelengths can only occur by the dissociation of BrOBr into BrO and Br. These products can either react back to BrOBr or rotate inside the matrix cages and react to BrBrO. Irradiation with light between 350 and 400 nm leads to a rapid conversion of BrOBr to BrBrO. This is in agreement with the MCQDPT calculations where the transition should occur at 399 nm. The calculated oscillator strength is—consistent with the fast observed isomerization at this wavelength—nearly 1 order of magnitude higher than those of the transition at 575 nm and leads to an excited state with B_2 symmetry. The energy of this state is high enough to overcome the barrier for the direct isomerization reaction, which appears to be the main reaction channel. The calculation of the IRC shows that the isomerization reaction would be efficiently activated if the energy would be transferred to the asymmetric stretching vibration, which also has B_2 symmetry, and partially to the bending vibration. Nevertheless, some additional dissociation into BrO and Br occurs. In case of isolated BrOBr molecules, the dissociation products will react either back into BrOBr or into BrBrO. During deposition of the BrOBr in the argon matrix, we did not ensure that all BrOBr molecules were isolated strictly and therefore surrounded only by argon, which results in the broad peak at 626 cm^{-1}. A certain amount of the molecules were isolated as dimers or were located at sites with other BrOBr molecules as neighbors. Dissociation of these molecules to BrO and O would allow the formation of BrO dimers and oxygen molecules, which explains the small BrO dimer peak observed in the spectra after irradiation of the matrix. There are more transitions from the BrOBr ground state to excited states with a relatively high oscillator strength. The energies of these excited states are so high that light with wavelengths of less than 250 nm are needed for the excitation. These wavelengths do not play an important role in the troposphere and lower stratosphere.

The energy of the lowest excited singlet state of BrBrO is only 1.10 eV above the ground state. Infrared light of 1126 nm is sufficient for the excitation. The extremely long irradiation times needed at these wavelengths to observe a change in the IR spectra are consistent with the very low calculated oscillator strength. The energy of this transition is not sufficient for the direct isomerization over the transition state which would require about 1.9 eV. The next few higher excited states would have enough energy for the transition. Nevertheless, the oscillator strengths of these transitions are extremely low. The experimental observation that the isomerization of BrBrO into BrOBr is faster than the reaction in the other direction when the matrix is irradiated with light below 340 nm is consistent with the calculation which predicts a relatively strong transition at 330 nm. The corresponding energy of 3.77 eV is much higher than that needed for the direct

TABLE 3: Vertical Exitation Energies of BrOBr and BrBrO Relative to the Ground States, Corresponding Excitation Wavelengths, and Oscillator Strengths of the Transitions

		excitation energies (eV)		excitation wavelength (nm)		oscillator strength for transition from ground state
multiplicity	state	CASSCF	MCQDPT2	CASSCF	MCQDPT2	
		BrOBr				
singlet	A_1	0	0			
	A_1	4.28	3.67	291	339	5.9×10^{-5}
	A_1	5.09	4.26	244	292	2.0×10^{-6}
	A_1	6.07	5.02	205	248	3.0×10^{-3}
	A_2	3.99	3.34	311	372	0
	A_2	4.75	3.95	262	315	0
	A_2	5.70	4.91	218	253	0
	B_1	3.83	3.11	325	399	7.0×10^{-3}
	B_1	6.14	5.45	202	228	1.2×10^{-5}
	B_1	6.89	5.74	180	217	0.11
	B_2	2.71	2.16	458	575	8.4×10^{-4}
	B_2	5.44	5.01	228	248	5.6×10^{-3}
	B_2	6.09	5.12	204	243	2.2×10^{-3}
triplet	A_1	3.36	2.92	370	425	0
	A_1	5.01	4.50	248	276	0
	A_1	6.67	5.89	186	211	0
	A_2	3.25	2.63	383	473	0
	A_2	4.49	3.83	277	325	0
	A_2	5.48	4.83	227	257	0
	B_1	3.27	2.61	380	477	0
	B_1	5.31	4.82	234	258	0
	B_1	5.60	4.88	222	255	0
	B_2	1.95	1.58	636	787	0
	B_2	5.09	4.64	244	268	0
	B_2	5.78	5.04	215	247	0
		BrBrO				
singlet		0	0			
		0.95	1.10	1308	1126	8×10^{-6}
		2.22	2.41	561	516	6×10^{-6}
		2.38	2.57	522	484	6×10^{-6}
		2.51	2.68	496	464	3×10^{-6}
		2.78	3.06	446	407	0
		4.05	3.77	307	330	7.9×10^{-2}
		4.77	3.89	261	320	7.7×10^{-4}
triplet		0.79	0.84	1567	1480	0
		1.32	1.68	944	739	0
		2.17	2.32	572	536	0
		2.29	2.39	544	519	0
		2.69	2.92	462	425	0
		2.78	2.99	446	415	0
		3.48	3.01	358	412	0
		4.99	4.59	249	271	0

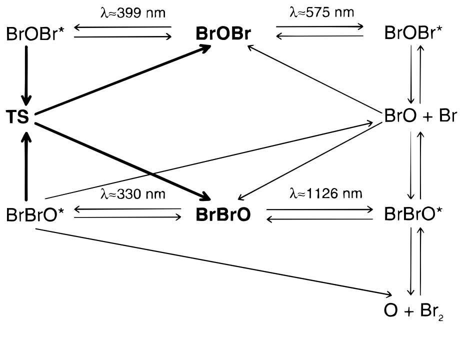

Figure 4. Schematic diagram of the possible reaction path for the isomerization of Br_2O. (The numbers in the diagram refer to the calculations.)

isomerization. Due to the excess energy, some of the molecules will dissociate. As shown in Figure 4 there are two reaction channels available for this dissociation. While one channel leads to BrO + Br, the other one will form bromine molecules and oxygen atoms. This reaction explains the observed product loss since bromine and oxygen are IR-inactive and thus cannot be detected in the IR spectra.

Our calculations are also very helpful for the interpretation of UV spectra of Br_2O in the literature. The spectrum from Levason et al.,[12] who measured a solid sample of Br_2O, is quite different from the gas-phase spectrum of Orlando and Burkholder,[14] even allowing for the fact that each was measured in a different phase. The spectrum of the solid sample shows a strong maximum at 213 nm, while the one of the gas phase shows the strongest absorption at 200 nm (which is the lower wavelength limit of this spectrum). These strong absorption features are in a good agreement with the calculated absorption band at 217 nm of BrOBr, which has a very strong oscillator strength. This band covers the absorption bands at 243 and 248 nm which are orders of magnitude weaker. Levason et al. reported a weak shoulder at 320.5 nm, whereas Orlando and Burkholder found a peak at 315 nm whose absorption is about 10 times weaker than that at 200 nm. The MCQDPT2 calculations do not show an excited state of BrOBr whose energy corresponds to this wavelength. However, the strongest calculated absorption band of BrBrO lies at 330 nm. Therefore, both UV spectra show that a mixture of BrOBr and BrBrO was measured. Since the photoisomerization is quite fast, it is also possible that the BrBrO was formed while measuring the UV spectra. Therefore, the amount of BrBrO may vary from the intensity of the light source and the measurement time.

Conclusion

In this contribution we described the light-induced reversible photoisomerization of BrOBr into BrBrO. Excellent agreement between experiments and calculations has been found in our studies. The results obtained allow one to set up a reaction scheme for the photoisomerization reaction, which is highly dependent upon the wavelength of the light used for irradiation. The calculations show that there is a transition state for the direct isomerization. With light below 400 nm, the reaction over the transition state results in a faster conversion. However, with lower energetic visible or infrared light the transition state cannot be reached and the conversion is possible only over the dissociation of the components. Further, the calculations were able to elucidate differences in the Br_2O UV spectra available in the literature.

Acknowledgment. This research was supported by the European Commisison within the LAMOCS project (#951104) (laboratory studies and modelling of heterogeneous chemistry in the stratosphere). Jennifer Kölm was supported by a stipend from Gottlieb Daimler- and Karl Benz-Stiftung and the German Academic Exchange Service (DAAD, Doktorandenstipendium HSP II, AUFE), which are gratefully acknowledged. This paper is contribution no. 1300 of the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven.

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