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FTIR Studies of the Reaction of $O(^{1}D)$ -Atoms with CF₃Br in Solid Argon Matrices

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The reaction $O(^1D) + CF_3Br$ has been investigated in solid Ar-matrices at T = 14 K. Codeposition of $O_3/CF_3Br/Ar$ mixtures and irradiation at 250 nm yielded F_2CO as dominant reaction product. Experiments with $^{18}O_3$ indicate that CF_3OBr was formed during the course of the reaction. Our observations were interpreted with the formation of an excited CF_3OBr molecule which can be stabilized in the matrix cage or decompose rapidly into two different F_2CO ·HF complexes.

1. INTRODUCTION

There is evidence of an increasing impact of the atmospheric bromine chemistry on the stratospheric ozone budget. From recent measurements on the vertical distribution of halons within the Innertropical Convergence Zone, it was concluded that CF_3Br (halon 1301) contributes about 13% to the total amount of bromine in the stratosphere [1]. Apart from direct photolysis, the fast reaction with $O(^1D)$ atoms $(4.0x10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [2]) is the main step initializing the photodecomposition and the release of Br-atoms within the stratosphere. It is possible that the primary step is $O(^1D)$ insertion into the C-Br bond. An analogous mechanism is favoured in $O(^1D)$ + alkane reactions [3]. However, there exist experimental findings indicating that formation of BrO and thus Br- abstraction from CF_3Br is the favoured primary step in the gas phase [4, 5]. The aim of this work was to get further information about the primary step of the reaction $O(^1D) + CF_3Br$ from matrix experiments, which allow the isolation and characterization of unstable intermediates.

2. EXPERIMENTAL

Aggregation and photoreaction of CF_3Br and ozone isolated in solid argon matrices has been studied by means of FTIR-spectroscopy in the frequency range between 4000 and 700 cm⁻¹ at a spectral resolution of 1.0 cm⁻¹. In these experiments the FTIR-spectrometer was used in the reflection mode. The matrices were prepared by depositing various $O_3/CF_3Br/Ar$ gas mixtures (1/2/1000 to 1/10/1000) with a rate of < 0.1 cm³/min through one injection inlet onto a gold coated metal substrate maintained at 14 K. The photolysis experiments were carried out with a 450 W high pressure Hg-Xe-lamp. An interference filter (250 nm, bandwidth at 0.5 peak transmission: 10 nm) was used, which allowed the selective photolysis of O_3 . The synthesis of ozone and its isotopes was performed by Tesla coil discharge.

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3. RESULTS AND DISCUSSION

In order to isolate 1:1 $CF_3Br\cdot O_3$ hetero-associates and to characterize their IR absorptions $CF_3Br/O_3/Ar$ matrices with mixing ratios between 1:10:1000 and 1:50:1000 were prepared. Weak band structures located at 1203.4 cm⁻¹ and 1192.6 cm⁻¹, corresponding to the red- and blue shifted v₄-band of CF_3Br , respectively, and the blue shifted v₃-band of ozone at 1044.0 cm⁻¹, indicated a weak $CF_3Br\cdot O_3$ interaction. In the case of CF_3I the interaction between CF_3I and O_3 turned out to be much stronger [6] due to the higher polarizability of the iodine atom. In accordance with the study of Andrews et al. [6], we associate these absorptions with a weak F_3C -Br·O₃ complex.

Selective photolysis of ozone at 250 nm produced O(¹D) atoms. Considering the slow relaxation of O(¹D) to O(³P) by the host matrix [7, 8] and the negligible rate coefficient $k(O(^{3}P)+CF_{3}Br)$ ($k(300K) = 2.1 \times 10^{-21} \text{ cm}^{3}\text{s}^{-1}$ [9]), the reaction O(³P) + CF₃Br was not important. The dominant reaction product was F₂CO, identified by the disturbed absorptions at 1940.6 cm⁻¹, 1912.5 cm⁻¹, 1241.5 cm⁻¹, 966.3 cm⁻¹, and 766.6 cm⁻¹. Obviously, F₂CO has been trapped essentially as a hetero-complex with FBr after formation. Annealing to 30 K resulted in a decay of these bands and a simultaneous increase of IR absorptions at 1963.0 cm⁻¹, 1887.3 cm⁻¹, 982.4 cm⁻¹, and 773.1 cm⁻¹ (table 1 and figure 1).

Table 1

Frequencies [cm⁻¹] of the observed different F₂CO·FBr complexes

F ₂ CO	F ₂ C ¹⁶ O (I)	F ₂ C ¹⁶ O (II)	F ₂ C ¹⁸ O (I)	F ₂ C ¹⁸ O (II)	assignment
1941.3	1940.6	1963.0	1907.6	1930.0	$2v_2$
1913.3	1912.5	1887.3	1878.7	1854.7	$\tilde{v_1}$
1237.6	1241.5		1240.7		V4
965.3	966.3	982.4	948.5	966.2	v_2
769.0	766.6	773.1			v_6^2

The strong opposite shifts between the v_2 and v_1 fundamentals substantially reduce the Fermi resonance, resulting in a much more pronounced v_1 band compared to the $2v_2$ band. A similar behaviour could be observed in the analogous CF₃I + O₃ system by Andrews et al. [6]. In agreement with the interpretation of these authors, we conclude that at first a less stable F₂CO FBr complex (I) was formed. Annealing causes an interconversion of this labile complex to the more stable complex II [6].

$F_2 \dot{C} = \dot{O}$	$F_2C = O_1$	
: F - Br	Br - F	
$F_2CO \cdot FBr$ complex I	$F_2CO \cdot FBr$ complex II	

Additionally, distinct absorption features could be observed at 1249.2 cm⁻¹, 1204.3 cm⁻¹, and 1193.0 cm⁻¹. From comparison with the fundamental modes of CF₃OF, CF₃OCl [10, 11], and CF₃OI [6], we conclude that CF₃OBr is an intermediate of the CF₃Br·O(¹D) interaction (table 2 and figure 2).

Table 2

Frequencies $[cm^{-1}]$ of CF₃OF, CF₃OCl, CF₃OBr, and CF₃OI in Ar-matrices (frequencies of CF₃¹⁸OBr and CF₃¹⁸OI in brackets).

CF ₃ OF	CF ₃ OCl	CF ₃ OBr	CF ₃ OI	assignment
1290	1268	1249.2 (1250.0)	1240.8 (1236.4)	C-Fantisym
1252	1219	1204.3 (1197.5)	1203.2 (1193.0)	C-F _{antisym}
1214	1200	1193.0 (1193.5)		C-F _{svm}
945	918	`	914.9 (896.7)	C-O _{str}



Figure 1. Matrix spectra of CF₃Br/¹⁸O₃/Ar =1:10:1000 (res. 1.0 cm⁻¹); (1) denotes the $2v_2$ and v_1 band of $F_2C^{18}O$, respectively, (2) the $F_2C^{18}O$ ·FBr complex (I) and (3) the more stable $F_2C^{18}O$ ·FBr complex (II). Lower trace: matrix spectra of $F_2C^{18}O$ /Ar, middle trace: reaction products after photolysis (250 nm, 1 hr) at 12 K and upper trace: same reaction mixture after annealing to 30 K.

Figure 2. F_3COBr (4) and $F_2CO \cdot FBr$ (I) (2) formation after photolysis (250 nm, 1 hr) of a CF_3Br/O_3/Ar = 1:10:1000 matrix, identified by the absorptions at 1249.2 cm⁻¹, 1204.3 cm⁻¹, and 1193.0 cm⁻¹ (4) and 1241.5 cm⁻¹ (2).

The results of our matrix experiments and comparable investigations on the $CFCl_3/O_3$ [12] and CF_3I/O_3 [6] system revealed a consistent pattern. As a remarkable difference to the gas phase experiments, there were no indications for IO or ClO formation in the respective reaction systems. Moreover, reaction pathways generating radicals have not been observed in the mentioned matrix studies. Our experiments provide strong evidence that CF₃OBr is an intermediate of the reaction $CF_3Br + O(^1D)$ in Ar-matrices. One possible explanation which could support the findings of the gas phase experiments would be a rapid recombination of the nascent BrO with the adjacent CF₃ radical in the Ar matrix cage. In this case, however, products of the competing reaction with O_2 (the photolysis product of ozone), particularily CF_3O_2 should have been observed. Alternatelively, a possible mechanism of the primary step could be an insertion reaction resulting in the highly excited intermediate CF_3OBr^* . The excess energy can partly be transferred to the host matrix or BrF elimination forms the final product F₂CO. In the CF₃I·O₃ system Andrews et al. [6] observed the primary formation of $CF_{3}IO$ at photolysis wavelength above 420 nm. The formation of $CF_{3}OI$ was explained by a light induced rearrangement of the iodosyl compound CF_3IO [6]. It should be noted that the quantum yield for $O(^{1}D)$ formation decreases sharply above 305 nm [13]. The iodosyl compound is most likely a product of the reaction of ground state $O(^{3}P)$ atoms with CF₃I. Photolysis experiments of these authors in a wavelength range where $O(^{1}D)$ production is dominant (between 240 and 420 nm) yielded nearly exclusively F₃C-O-I. Thus we conclude that in our experiments the reaction $O(^{1}D) + CF_{3}Br$ proceeds directly via $CF_{3}OBr$ formation and not via a F₃CBrO intermediate.

It is obvious, that the rather different conditions in solid Ar - matrices compared to the gas phase (low temperature, cage effects, rapid relaxation of excited molecules by the host matrix) can favour different reaction mechanisms and products. In the gas phase the highly excited nascent CF_3OBr^* will decompose nearly instantly to secondary products, whereas in the matrix cage FBr elimination from CF_3OBr seems to be the dominant secondary step.

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