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MATRIX ISOLATION STUDY OF THE PHOTOLYSIS OF CF_2Br_2. INFRARED SPECTRUM OF THE CF_2Br FREE RADICAL

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Absorptions which appear at 684, 1138, and 1198 cm^{-1} upon photolysis of CF_2Br_2 isolated in an argon matrix at 14 K by 2537- or 1216-Å radiation have been assigned to the three stretching fundamentals of the CF_2Br free radical. Several of the vibrational fundamentals of $^{13}CF_2Br_2$ have been identified in the infrared spectra of unphotolyzed deposits. Photolysis processes which may occur under the conditions of these experiments are discussed.

1. Introduction

Earlier matrix isolation studies in this laboratory have led to the first infrared identification of the CF_3 [1,2] and CF_2Cl [3] free radicals. In the course of a recent study of the products of the reaction of excited argon atoms with the tetrahalomethanes, it became necessary also to obtain the infrared spectrum of the CF_2Br free radical, not previously reported. Although the flash photolysis studies of Mann and Thrush [4] and of Simons and Yarwood [5] had shown that CF_2Br_2 was an excellent photolytic source of CF_2, subsequent studies by Walton [6] of the 2650-Å photolysis of CF_2Br_2 and by Tedder and Walton [7] of the 2537- and 2650-Å photolysis of CF_2Br_2 in the presence of ethylene or of one of the fluoroethylenes were consistent with the primary photodecomposition of CF_2Br_2 at these wavelengths to produce CF_2Br + Br as the sole products.

As will be shown in the following discussion, CF_2Br can be stabilized in sufficient concentration upon 2537- and 1216-Å photolysis of CF_2Br_2 isolated in an argon matrix at 14 K for direct infrared detection of all three stretching fundamentals. This identification is of interest not only because the spectrum of CF_2Br has not previously been reported but also because of widespread recent concern with the environmental implications of the photodecomposition of bromine-containing molecules in the atmosphere and in the lower stratosphere.

2. Experimental details

The CF_2Br_2 sample (Matheson Co., Inc.) used for these experiments was freed of more volatile trace impurities by repeated condensation at 77 K and pumping on the solid sample. Teh argon (Matheson Co., Inc.) used as matrix material was not subjected to further purification. Samples were prepared using standard manometric procedures.

The cryogenic equipment and optical configuration used for infrared spectroscopic observation of the sample deposit have previously been described [8]. After the infrared spectrum of an Ar : CF_2Br_2 deposit with a mole ratio of 270 had been obtained, the entire solid sample, maintained at 14 K, was irradiated with the full light of a medium pressure mercury arc. Studies of the vacuum ultraviolet photolysis of an Ar : CF_2Br_2 = 400 sample at 14 K were also conducted, using a hydrogen discharge lamp and photolysis procedures which have previously been described [9].

Infrared spectra were recorded between 400 and 1600 cm^{-1} using a Beckman IR-9 infrared spectrophotometer. Under the scanning conditions typical of these experiments, the resolution and the relative and absolute frequency accuracies are estimated to be 1 cm^{-1} over the spectral region which was observed.

3. Observations and discussion

The infrared spectrum between 500 and 1500 cm^{-1} of an unphotolyzed Ar : CF_2Br_2 = 270 deposit at 14 K is shown in the solid trace of fig. 1. With minor exceptions, all of the absorptions present in this spectrum lie within a few cm^{-1} of the band centers reported by Plyler and Acquista [10] for the infrared absorptions of CF_2Br_2 in the gas phase.

The ν_3 fundamental, which appears in the gas phase at 621 cm^{-1}, has as its counterpart in an argon matrix two equally intense absorptions at 622 and 627 cm^{-1}. In observations on smaller Ar : CF_2Br_2 deposits, the very prominent ν_1 absorption, which appears in the gas phase at 1088 cm^{-1}, is split into two equally intense components at 1081 and 1085 cm^{-1} and a much less intense absorption at 1096 cm^{-1}. Similarly, the ν_8 absorption, with the gas phase band center at 1150 cm^{-1}, appears in an argon matrix as a pair of equally intense, very prominent absorptions at 1142 and 1146 cm^{-1}, with a poorly resolved, much less intense satellite absorption at 1162 cm^{-1}. Such splittings frequently occur for molecules isolated in rare-gas matrices and may be attributed to the trapping of the molecule in different types of site in the rare-gas lattice. In the Ar : CF_2Br_2 experiments, they are helpful in the assignment of several of the less intense peaks characteristic of thick sample deposits.

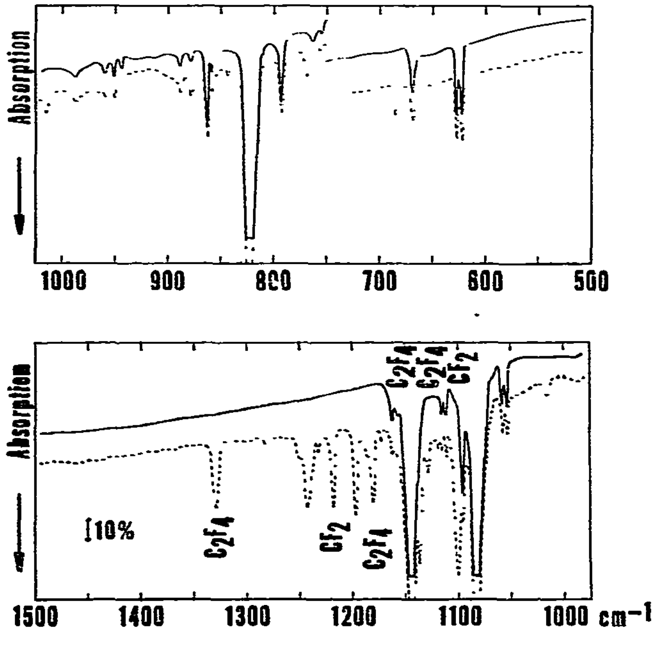

Fig. 1. Ar : CF_2Br_2 = 270. 14 K. —— 24.1 μmol CF_2Br_2 deposited over period of 320 min, without photolysis. - - - Total deposit exposed for 51 min to full light of a medium pressure mercury arc.

The relative intensities of the two weak absorptions at 1054 and 1058 cm^{-1} and their separation from the very strong 1081–1085 cm^{-1} absorptions, assigned to the totally symmetric C–F stretching fundamental (ν_1), suggest the assignment of the 1054–1058 cm^{-1} peaks to ν_1 of $^{13}CF_2Br_2$. Similarly, the 1112 and 1115 cm^{-1} pair of absorptions may be assigned to the antisymmetric C–F stretching fundamental (ν_8) of $^{13}CF_2Br_2$ present in natural abundance. The correspondence of the contour of the 1112–1115 cm^{-1} pair of absorptions to that of the 1142–1146 cm^{-1} pair of absorptions (observed in a small deposit) suggests that the 1122 cm^{-1} ($\nu_5 + \nu_6$) combination band of the gas phase experiments is too weak to be observed in the present studies.

The antisymmetric C–Br stretching fundamental (ν_6), which appears in the gas phase as the very prominent absorption at 829 cm^{-1}, appears in an argon matrix as a single very strong absorption at 822 cm^{-1} The separation of the much weaker absorption at 792 cm^{-1} is appropriate for the assignment of this peak to $^{13}CF_2Br_2$. Plyler and Acquista [10] have assigned a weak gas phase absorption at 800 cm^{-1} to the ($\nu_2 + \nu_3$) combination band, calculated from their data to lie at 786 cm^{-1}. Since within experimental error the separation between this peak and the very prominent $^{12}CF_2Br_2$ fundamental absorption is the same in both the gas phase and the argon matrix observations and since this separation is close to the expected carbon-13 shift in a C–Br stretching fundamental, the alternate assignment of the 800 cm^{-1} gas phase absorption to the ν_6 fundamental of $^{13}CF_2Br_2$ is suggested.

The moderately intense 663 cm^{-1} absorption can be assigned to the $2\nu_7$ overtone band, which lies at 662 cm^{-1} in the gas phase. Of the remainig peaks, only the moderately intense peak at 862 cm^{-1} and the much weaker ones at 878 and 887 cm^{-1} cannot be assigned to CF_2Br_2. (A gas phase absorption at 875 cm^{-1} was assigned to the ($\nu_8 - \nu_5$) difference band, which should be undetectable at 14 K.) These three peaks correspond exactly in position and relative intensities to prominent absorptions observed in this laboratory for CF_2ClBr isolated in an argon matrix. Two other strong absorptions of this molecule, associated with the C–F stretching vibrations, would be overlapped by the corresponding absorptions of CF_2Br_2.

As is shown by the broken-line trace of fig. 1, several prominent absorptions appeared when samples of CF_2Br_2 isolated in an argon matrix were exposed to the full light of a medium-pressure mercury arc. The positions and peak optical densities of these absorptions are compared with those of product absorptions observed on 1216-Å photolysis of CF_2Br_2 in table 1. Absorptions at 1101 and 1219 cm^{-1} are readily assigned to CF_2 and absorptions at 1129, 1180, and 1330 cm^{-1} to C_2F_4 isolated in an argon matrix [11]. Another C_2F_4 absorption, at 1164 cm^{-1}, is partly obscured by a CF_2Br_2 absorption. Comparison with the liquid-phase data reported by Kagarise and Daasch [12] for $(CF_2Br)_2$ suggests the assignment of peaks at 769, 877, 1014, 1173, and 1244 cm^{-1} to this product. Another weak $(CF_2Br)_2$ absorption may overlap that of C_2F_4 at 1129 cm^{-1}. In the 2537-Å photolysis studies, the 1101-cm^{-1} absorption of CF_2 appeared as a shoulder on the very prominent 1096 cm^{-1} absorption of unphotolyzed CF_2Br_2, considerably enhancing the uncertainty in the peak optical density of this CF_2 absorption. Comparison of the peak optical densities of the 1219 cm^{-1} CF_2 absorption indicates that a higher yield of CF_2 was obtained in the 1216-Å photolysis experiment of table 1 than in the 2537-Å photolysis experiment. On the other hand, the yields of C_2F_4 and of $(CF_2Br)_2$ were substantially smaller in the 1216-Å photolysis experiment than in the 2537-Å photolysis experiment. Although the yields of products containing two carbon atoms would be expected to be somewhat lower in experiments on samples of mole ratio 400 (as in the 1216-Å study) than in experiments using a mole ratio of 270 (as in the 2537-Å study), the observed difference was considerably greater than might be expected on the basis of the difference in mole ratios alone.

Table 1
Absorptions [a] which appear between 400 and 1600 cm^{-1} following photolysis of CF_2Br_2 isolated in an argon matrix by 2537- or 1216-Å radiation

cm^{-1}	Peak optical density		Assignment
	2537 Å	1216 Å	
414	0.054	0.037	
684	0.075	0.071	CF_2Br
769	0.061	0.038	$(CF_2Br)_2$
877	0.030	–	$(CF_2Br)_2$
1014	0.051	–	$(CF_2Br)_2$
1101	0.785	0.712	CF_2
1123	–	0.031	
1129	0.074	0.038	C_2F_4, $(CF_2Br)_2$
1138	sh	0.446	CF_2Br
1173	0.028	–	$(CF_2Br)_2$
1180	0.234	0.069	C_2F_4
1187	–	0.069	
1198	0.287	0.326	CF_2Br
1219	0.261	0.381	CF_2
1233	sh	sh	
1244	0.249	0.111	$(CF_2Br)_2$
1250	sh	sh	
1330	0.238	0.074	C_2F_4

[a] sh = shoulder.

Of the four remaining absorptions common to both photolysis experiments, two, at 684 and 1198 cm^{-1}, had quite similar optical densities in the two systems. The photometry of the broad 414-cm^{-1} absorption, which lies in a region of poor spectrometer response, was relatively uncertain. A fourth prominent absorption, at 1138 cm^{-1}, appeared as a low-frequency shoulder on the very strong 1146 cm^{-1} CF_2Br_2 absorption in the 2537-Å photolysis studies. (The CF_2Br_2 absorptions were much weaker in the 1216-Å photolysis experiments, in which it was necessary to conduct the deposition and the photolysis concurrently.)

If the photolysis were to have proceeded by the formation of CF_2 alone, the only products to be expected at the mole ratios here employed would be CF_2, C_2F_4, and $(CF_2Br)_2$, which conceivably might be formed by the reaction of CF_2 with CF_2Br_2 trapped in an adjacent site in the argon lattice or by bromine-atom scavenging by C_2F_4. The gas phase photolysis studies at 2537 and 2650 Å [6,7] have indicated that at these wavelengths CF_2Br is formed in the primary photodecomposition. If the Br atoms have a significant probability of diffusing from the site of their photoproduction rather than reacting with CF_2Br to re-form CF_2Br_2 and if CF_2Br is reasonably photolytically stable, it should also be observed in the matrix experiments. The prominent product absorptions at 1138 and 1198 cm^{-1} can reasonably be assigned to the two C–F stretching fundamentals of CF_2Br; the corresponding fundamentals of CF_2Cl [3] lie at 1148 and 1208 cm^{-1}. Unfortunately, the matrix data do not provide definitive information on the symmetries of the C–F stretching fundamentals of either molecule. The 684 cm^{-1} absorption is in a region typical of C–Br stretching fundamentals, which generally are rather strongly absorbing. Since the C–Cl stretching absorption of CF_2Cl lies at 761 cm^{-1}, in the range typical for such absorptions, and since the bonding properties of CF_2Br are expected to be similar to those of CF_2Cl, the assignment of the 684 cm^{-1} peak to the C–Br stretching fundamental of CF_2Br is also reasonable. Although the 414 cm^{-1} absorption may be contributed by an FCBr deformation vibration of CF_2Br, this absorption is relatively weak and broad, making its assignment much less certain than that of the other absorptions typical of the matrix experiments.

The ultraviolet absorption spectrum reported by Walton [6] for CF_2Br_2 showed a gradual onset, with a maximum at 2280 Å and with no structure. The molar extinction coefficient at 3000 Å was more than a hundred times smaller than that at 2650 Å. In an experiment in which the Ar : CF_2Br_2 deposit was exposed to filtered mercury-arc radiation with a short wavelength cutoff of 3000 Å, no products resulted, consistent with Walton's absorption data. Although CF_2 may be formed by photodecomposition of the initially formed CF_2Br in the 2537-Å photolysis experiments, the present experiments have yielded no information on the wavelength range in which photodecomposition of CF_2Br occurs. Since prominent CF_2Br absorptions were also observed in the 1216-Å photolysis studies, the primary photodecomposition of CF_2Br_2 to form CF_2Br + Br is likely to play an important role in the vacuum-ultraviolet region, as well. The present experiments cannot determine whether CF_2 is formed in a primary photodecomposition process at 1216-Å or whether it is formed predominantly by the photodecomposition of CF_2Br.

Previous matrix isolation experiments have yielded very little information on the extent to which the heavy bromine atom can diffuse through the argon lattice at 14 K. The B–X absorption bands of CN were observed in the ultraviolet spectrum of Ar : BrCN samples which had been deposited at 14 K with concurrent 1216-Å photolysis, but there was a pronounced decrease in the CN product yield as the mass of the halogen atom was increased, and a very prominent infrared absorption in the BrCN photolysis experiments could be assigned to BrNC [13]. The appearance of prominent absorptions of both CF_2Br and CF_2 in the present experiments suggests that the Br atom has a significant probability of diffusing from the site of its photoproduction in an argon lattice at 14 K.

The quantum yield measurements of Walton [6] suggested that the initial photoprocess at 2650-Å resulted in the formation of an excited CF_2Br_2 molecule which could either decompose into CF_2Br + Br or be collisionally deactivated at higher sample pressures. The stabilization of CF_2Br in the argon matrix experiments requires that the lifetime of excited CF_2Br_2 trapped in solid argon at 14 K be sufficiently long for its dissociation to be competitive with deactivation by the matrix.

4. Conclusions

Photolysis of CF_2Br_2 isolated at 14 K in an argon matrix by either 2573- or 1216-Å radiation leads to the stabilization of CF_2Br, requiring that bromine atoms have a significant probability of diffusing from the site of their photoproduction. The C–Br stretching fundamental absorption of CF_2Br appears at 684 cm^{-1} and the two C–F stretching fundamental absorptions at 1138 and 1198 cm^{-1}.

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