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Bromodifluoroacetyl fluoride, $CF_2BrC(O)F$: Experimental and theoretical studies

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Abstract

Bromodifluoroacetyl fluoride, $CF_2BrC(O)F$, was prepared through the gas-phase reaction of bromotrifluoroethene, CF_2CFBr, with molecular oxygen initiated either by NO_2 or CF_3OF. The compound was experimentally studied by FTIR spectroscopy of the gas phase and also isolated in Ar and N_2 matrices at low temperature. The energy differences between the possible conformers were theoretically studied, as well as the vibrational spectra of the conformers.

Keywords: Conformational analysis; Matrix isolation; FTIR spectroscopy; Theoretical calculations; Bromodifluoroacetyl fluoride; Gas-phase reaction

1. Introduction

Several halodifluoroacetyl halides of the type $CF_2XC(O)Y$, with X, Y = halogen, have been subject of conformational and vibrational studies during the last years. $CF_2ClC(O)F$ [1], $CF_2ClC(O)Cl$ [2], and $CF_2BrC(O)Cl$ [3] have been found to present predominantly the *gauche* conformation in equilibrium with the less stable *anti* conformer (X atom oriented *anti* to Y atom). As far as we know, there is no report in the literature about the bromodifluoroacetyl fluoride, $CF_2BrC(O)F$.

Here we present the preparation of bromodifluoroacetyl fluoride, $CF_2BrC(O)F$, through the gas-phase reaction of bromotrifluoroethene, CF_2CFBr, with molecular oxygen initiated either by NO_2 or CF_3OF. The compound was experimentally studied by FTIR spectroscopy of the gas phase and also as isolated in an inert matrix environment at low temperature. Theoretical calculations were performed in order to determine the energy differences between the possible conformers and also to predict the vibrational spectra of these conformers and thus help in the correct assignment of the vibrational absorptions.

2. Experimental

The bromodifluoroacetyl fluoride, $CF_2BrC(O)F$, was produced as the main product of the thermal gas-phase oxidation of bromotrifluoroethene, CF_2CFBr, with molecular oxygen initiated either by the addition of NO_2 [4] or CF_3OF to the double bond of the alkene.

All reactants were purchased commercially. NO was eliminated from NO_2 (Matheson 99.5%) by a series of freeze–pump–thaw cycles in presence of O_2 until disappearance of the characteristic blue colour of N_2O_3. Finally, the degassed NO_2 was purified by fractional condensation using the fraction that distilled between 213 and 243 K. CF_3OF (PCR, 97–98%) was washed with 0.1 mol dm^{-3} NaOH and filtered at 80 K [5]. The CF_2CFBr (PCR, 97–98%) contained CF_4, and CF_3CF_3 as impurities. These impurities are more volatile than CF_2CFBr, but, as distilling together could not be separated by fractional condensation. The CF_2CFBr was purified by intermittent brief

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evacuation cycles at 153 K, opening and closing the trap valve. This procedure was repeated several times, until the disappearance of the respective very strong absorption bands of CF_4 [6] and CF_3CF_3 [7] at 1279 and 1250 cm^{-1}, respectively, in the IR spectrum of CF_2CFBr. Oxygen (La Oxígena 99.99%) was bubbled through 98% analytical-grade H_2SO_4 and passed slowly through a Pyrex coil at 153 K.

The experiments were performed in a grease-free conventional static system, allowing pressure measurements at constant volume and temperature. A spherical quartz bulb of 270 cm [3] was used as reaction vessel. The pressure was measured with a quartz spiral gauge.

Infrared spectra of the reaction mixtures were recorded on Shimadzu IR-435 spectrometer. The gas and matrix-isolated FTIR spectra of $CF_2BrC(O)F$ were recorded on a Nexus Nicolet instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000–400 or 600–200 cm^{-1}, respectively). The gas FTIR spectra were recorded at ambient temperature using 10 cm cell provided with KBr windows with a 0.5 cm^{-1} resolution.

Gas mixtures of $CF_2BrC(O)F$ with Ar and N_2 (both AGA) in the proportion ca. 1:1000, prepared by standard manometric methods, were deposited on a CsI window cooled to ca. 10 K by means of a Displex closed-cycle refrigerator (SHI-APD Cryogenics, Model DE-202) using the pulse deposition technique [8,9].

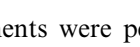
Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV–visible radiation ($200 \leqslant \lambda \leqslant 800$ nm) from a Spectra-Physics Hg–Xe arc lamp operating at 1000 W. The output from the lamp was limited by a water filter to absorb IR radiation and so minimize any heating effects. The IR spectrum of the matrix with a 0.125 cm^{-1} resolution was then recorded at different times of irradiation in order to monitor closely any change in the spectra. The UV–visible spectra of the products in the gas phase were recorded on a Hewlett–Packard Model 8452A spectrometer, using a 10 cm quartz cell.

All of the quantum chemical calculations were performed using the Gaussian 98 [10] program system under the Linda parallel execution environment using two coupled PCs. Geometry optimizations were sought using standard gradient techniques by simultaneous relaxation of all the geometrical parameters. The calculated vibrational properties correspond in all cases to potential energy minima for which no imaginary vibrational frequency was found.

3. Preparation of bromodifluoroacetyl fluoride, $CF_2BrC(O)F$

3.1. Gas-phase reaction between NO_2, CF_2CFBr and O_2

The experiments were made at 313.4 K. The initial pressure of CF_2CFBr was varied between 18.8 and 43.9 Torr, that of NO_2 between 0.9 and 4.8 Torr and that of O_2 between 96.9 and 402.9 Torr. All experiments were carried out to the complete consumption of alkene. After all CF_2CFBr was consumed a slow pressure increase and the formation of Br_2 were observed.

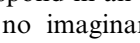
The main reaction product was $CF_2BrC(O)F$. Its yields, based on the initial pressure of the alkene, increased from 79% to 85% as the pressure of NO_2 decreased from 4.8 to 0.9 Torr. Minor quantities of $C(O)F_2$ and C(O)FBr, and small amounts of $CF_2BrCFBrO_2NO_2$ and trifluorobromoethene epoxide (TFBrEO),  , were also formed. The compounds $C(O)F_2$ [11] and C(O)FBr [12,13] were identified by their respective IR spectra. The formation of C(O)FBr was also detected by its UV spectrum in the range of 200–220 nm [13]. The product $CF_2BrCFBrO_2NO_2$ was identified by its infrared absorption band at 1758 cm^{-1}, characteristic to the NO_2 group of the haloalkylperoxynitrates and haloalkoxylperoxynitrate, appearing between 1754 and 1762 cm^{-1}. The trifluorobromoethene epoxide (TFBrEO), was identified in the reaction mixture by its infrared band at 1540 cm^{-1}, assigned to the ring-breathing mode, that is characteristic of fluoroepoxides. This band appears at 1500 cm^{-1} for 1,1-dichloro-2,2-difluoroethene epoxide [14], at 1550 cm^{-1} for chlorotrifluoroethene epoxide [14] and at 1551 cm^{-1} for perfluoropropene epoxide [15].

To obtain pure $CF_2BrC(O)F$, the reaction mixture in the reaction vessel was rapidly cooled to liquid air temperature and the mixture separated by fractional condensation. The fraction volatile between 158 and 183 K was $CF_2BrC(O)F$. The fractions of eight experiments were collected together to obtain major amount of bromodifluoroacetyl fluoride.

3.2. Gas-phase reaction between CF_3OF, F_2CFBr and O_2

The experiments were made at 273, 253.5 and 239 K. The initial pressure of CF_3OF was varied between 0.9 and 2.4 Torr, that of CF_2CFBr between 11.5 and 30.7 Torr and that of O_2 between 48.2 and 100.7 Torr.

At 273 K the reaction was completed in 10 min. At 253.5 and 239 K the time of permanence of the reaction system $CF_3OF + CF_2CFBr + O_2$ in the reaction vessel was between 42 and 121 min. In all runs the CF_2CFBr was completely consumed.

The main product was $CF_2BrC(O)F$ (yields 81–95% based on the CF_2CFBr consumed). Minor quantities of $C(O)F_2$ and C(O)FBr, and traces of $CF_3OCF_2C(O)F$ and bromotrifluoroethene epoxide  were also formed. $CF_3OCF_2C(O)F$ was identified by its IR spectrum [16].

The very strong absorption band of CF_3OOCF_3 at 1166 cm^{-1} [17] and that at 1122–1119 cm^{-1}, characteristic of $CF_3C(O)F$ [18], were not observed.

To determine the concentration of $CF_2BrC(O)F$, the room temperature infrared calibration curve was made, allowing conversion of the absorption intensities at 1887 cm^{-1} to the pressure of $CF_2BrC(O)F$. The pressure corresponding to the temperature of each run was calculated starting from the pressure of this compound at room temperature obtained from the calibration curve.