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FTIR spectroscopic study of 1,1,1-trifluoro-2-chloroethyl and 1,1,1-trifluoro-2-chloroethylperoxyl radicals

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Abstract

A combination of matrix isolation and FTIR spectroscopy was applied to investigate 1,1,1-trifluoro-2-chloroethyl (1) and 1,1,1-trifluoro-2-chloroethylperoxyl (2) radicals. Radical 2 was obtained by vacuum pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane (3). Corresponding peroxyl radicals was generated by co-condensation of pyrolysis products and molecular oxygen in an argon matrix. To assign the experimental bands DFT calculations (B3LYP/6–311G**) were carried out. The fundamental bands of O–O and C–O stretching vibrations of peroxyl radical CF₃CHClOO (1102.1, 972.7, cm⁻¹) were identified by their red shifts to 1044.7 and 954.1 cm⁻¹ in the spectra of ¹⁸O substituted derivatives. UV photolysis of the radical 2 in the low-temperature matrix produced difluoroformaldehyde CF₂O, radicals ClCO, CF₃, as well as CO and HCl as the primary photoproducts. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: 1,1,1-trifluoro-2-chloroethyl radical; 1,1,1-trifluoro-2-chloroethylperoxyl radical; Pyrolysis; Photolysis; Matrix isolation; IR spectroscopy

1. Introduction

A wide class of atmospherically important chemical reactions involves fluorine-containing free radicals as intermediate species. Generally, in chemical studies their participation is monitored indirectly via the chemical kinetics or analysis of stable reaction products [1-3]. A combination of matrix isolation and IR spectroscopy was successfully used for direct observation of primary intermediates and to study of their structure. Radicals **1** and **2** were predicted to exist by the theoretical calculations [4] and were suggested on the basis of the UV spectroscopic study of the reactions of CF_3CH_2CI with fluorine atoms [3]. However, reliable vibration para-

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meters of these species have not been obtained until quite recently. The purpose of this work is the IR spectroscopic study of radicals 1 and 2 stabilized in argon matrices.

2. Experimental

Radicals 1 were generated by the thermolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane (3) at 1150–1300 K and 10^{-4} Torr in a 50–120 mm quartz reactor (5 mm in diameter) attached to an optical helium cryostat. The pyrolysis products were co-deposited with excess of argon on the copper mirror cooled to 12 K by a closed cycle cryogenic system Displex 208R (Air Products & Chemicals). To form corresponding peroxyl radicals **2**, radicals **1** were allowed to react with argon matrices containing from 1 to 10%

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Fig. 1. IR spectra of 1,1,1-trifluoro-2-chloroethyl (1) and of 1,1,1-trifluoro-2-chloroethyl peroxyl (2) radicals in an argon matrix at 12 K: (a) spectrum of pyrolysis products of 1,1,1-trifluoro-2-bromo-2-chloroethane; bands of radical 1 are denoted by asterisk; letters E designate bands of trifloroethylene; (b) spectrum of the products of the reaction chloroethyl radical with oxygen, bands of radical 2 are denoted by arrows.

oxygen during the trapping process. IR spectra in the region 4000–450 cm⁻¹ were recorded with a FTIR-spectrometer Bruker IFS-113 v (1 cm⁻¹ resolution) by the beam reflection scheme. The UV photolysis ($\lambda > 250$ nm) was carried out by a high-pressure mercury lamp (1000 W). Commercial **3** and isotope-substituted ¹⁸O₂ of 99% purity with 82% isotope saturation were used without additional purification.

Quantum chemical calculations of molecular structure and vibrational spectra were performed by ab initio (UHF) and density functional theory (B3LYP) approximations using Caussian 94 program package [5] on a Power Challenge supercomputer at the Computer Assistance of the Chemical Research Center of the Russian Academy of Sciences.

3. Results and discussion

In the IR spectrum of matrix isolated products of the pyrolysis precursor **3**, two groups of new bands are observed along with the bands of the starting compound (Fig. 1a, Table 1). The first one corresponds to the stable trifluoroethylene: 3158.2, Table 1

Experimental and calculated (B3LYP/6-311G**) vibrational frequencies of 1,1,1-trifluoro-chloroethyl radical in the 4000–450 $\rm cm^{-1}$ range

Preliminary, assignment	Exp. ν , cm ⁻¹	Int.	Calc. ν , cm ⁻¹	Int.(km/mol)
ν CH	3118.3	W	3245.6	3
δ HCC, ν_s CF ₃	1353.3	s	1354.5	102
$\nu_{\rm s} {\rm CF}_3$	1237.6	s	1245.0	169
$\nu_{\rm as} \rm CF_3$	1147.2	vs	1145.8	245
$\nu_{\rm as} \rm CF_3$	1129.6	vs	1121.3	323
ν C–C, δ HCC	943.3	m	934.2	94
ν C–Cl, δ HCC	824.7	w	818.8	19
$\delta_s CF_3$	654.9	w	648.8	22
wHCCl, $\delta_s CF_3$	572.0	vw	565.0	6
$\delta_{as}CF_3$	539.0	vw	532.1	4

1781.0, 1354.7, 1257.7, 1172.4, 924.9, 753.5 cm⁻¹ [6]. The second set contains 10 bands assigned to a labile species. As should be expected, these bands decreased in intensity when matrix was heated up to 35-37 K, resulted in a diffusion of molecules and simultaneous growth of intensities of bands of (CF₃CHCl)₂- the dimerization product of radical **1**. Similar products were detected previously [7] under laser radiolysis of **3**. This fact allowed us to assign the last set of the bands to radical **1** and showed that the thermal decomposition of the precursor **3** occurs via two pathways: to form the trifluorochloroethyl radical or trifluoromethylcarbene which isomerized to Ar matrix, 12 K



trifluoroethylene. It was found that the CF_3CHCl radical is generated at the first step of the reaction (at lower temperature and in shorter pyrolysis tube). It could be explained by the successive cleavage of the C–Br and C–Cl bonds (Scheme 1).

It is known [8,9] that the reaction of free radicals with O_2 results in the formation of peroxyl radicals (Scheme 1). Co-condensation of pyrolysis product of **3** with dioxygen (Scheme 1) lead to appearance of new bands (Fig. 1b, Table 2). Intensities of these signals were changed simultaneously when the matrix was heated to the diffusion temperature (35 K) or under UV irradiation. This fact and the presence of the bands, that showed oxygen frequency shifts upon substitution of ${}^{16}O_2$ with ${}^{18}O_2$ confirmed the assignment of latter species to radical **2**.

The full assignment of experimental bands was performed by comparison of quantum chemical calculated and experimental FTIR spectra of radicals **1** and

Table 2

Experimental and calculated (B3LYP/6-311G**) vibrational frequencies of 1,1,1-trifluoro-2-chloroethyl peroxyl radical in the $4000-450 \text{ cm}^{-1}$ range

Preliminary assignment	$CF_3CHCl^{16}O^{16}O(\nu, \text{ cm}^{-1})$		$CF_{3}CHCl^{18}O^{18}O(\nu, cm^{-1})$		
	Exp.	Calc.	Exp.	Calc.	
νCH	3023.9	3150.3	3024.1	3150.0	
δΗCC	1343.3	1355.2	1345.0	1353.8	
$\nu_{\rm as} \rm CF_3$		1302.5		1300.8	
$\nu_{\rm as} \rm CF_3$	1275.6	1273.4	1274.6	1273.2	
$\nu_{\rm s} {\rm CF}_3$	1210.3, 1204.9	1205.5	1209.1,1203.8	1202.1	
δ HCCl, ν O–O	1155.9, 1154.3	1163.9	1155.3, 1154.0	1153.7	
ν O–O, δ HCCl	1102.1	1143.6	1044.7	1091.5	
ν C–O	972.7	975.3	954.1	955.0	
ν C–C, δ HCO	887.3	883.4	886.2	882.3	
ν C–Cl	854.4	812.9	849.4	811.8	
δ HCO, ν C–C	703.3, 686.8	699.1	701.2, 685.2	697.3	
		560.0		556.9	
		544.6		542.4	



Fig. 2. DFT B3LYP/6–311G** calculated geometries of minimum energy structure of 1,1,1-trifluoro-2-chloroethyl (1) and of 1,1,1-trifluoro-2-chloroethyl peroxyl (2) radicals.

2. Geometry were optimized by UHF and B3LYP methods with 3-21G, $6-31G^{**}$ and $6-311G^{**}$ basis sets. The best agreement of calculated and experimental data was achieved at the B3LYP/6- $311G^{**}$ level (Tables 1 and 2).

According to the results of calculations radical 1 has gauche-conformation and belongs to C_1 symmetry group (Fig. 2). All 15 vibrations are active in the IR spectrum. We observed 10 absorption bands that characterize all vibrations in the 4000-450 cm⁻¹ range. High frequency at 3118.3 cm⁻¹ is assigned to the CH stretching vibration and lies in nominal range for CH stretches at sp² electronic configuration of carbon. This fact was confirmed by the calculations, which show shortening of C-H bond at CHCl group (Fig. 2). The bands observed at frequencies lower than 1400 cm^{-1} are non-characteristic and the vibrations have a mixed character. The assignment was made on the base of published data and visualization of the calculated frequencies and shapes of vibrations by MOLDRAW program [10].

The minimum energy conformer of radical **2** belongs to C_1 -symmetry (Fig. 2). Calculated spectrum of **2** exhibits 21 normal vibrations, 13 of which lie in the 4000–450 cm⁻¹ region. Weak band at 3023.9 cm⁻¹ were assigned to C–H stretching vibration. The characteristic bands of O–O and C–O stretching vibrations of radical **2** (1102.1 and 972.7 cm⁻¹) were identified by their red shifts to 1044.7 and 954.1 cm⁻¹ respectively in the spectra of ¹⁸O substituted derivatives.

The appearance of doublets at 1210.3, 1204.9 cm⁻¹ and at 1155.9, 1154.3 cm⁻¹ can be explained by the matrix effects. One of addition band at ca. 700 cm⁻¹ is likely an overtone of lower vibrations.

The UV photolysis ($\lambda > 250$ nm) of the radical CF₃CHClOO in the low-temperature matrix produced difluoroformaldehyde CF₂O (1939.6, 1907.3, 1236.7, and 773.1 cm⁻¹) [11], radicals ClCO (1879.5 cm⁻¹) [12], CF₃ (1250.0, 1082.7 cm⁻¹) [13], as well as CO and HCl (2150.8 and 2846.6 cm⁻¹) [14], as primary photoproducts.

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