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# High-vacuum pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane. IR spectrum of 1,1,1-trifluoro-2-chloroethyl radical in an argon matrix

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The products of high-vacuum pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane were studied by matrix IR spectroscopy. The decomposition of 1,1,1-trifluoro-2-bromo-2-chloroethane was shown to occur predominantly via two directions: to form the 1,1,1-trifluoro-2-chloroethyl radical and trifluoromethylcarbene isomerizing to trifluoro-ethylene. The CF<sub>3</sub>CHCl radical has been detected in the matrix for the first time. The bands observed in the IR spectrum were calculated by the quantum-chemical B3LYP/6-311G(d,p) method and assigned to normal vibrations of the radical.

Key words: 1,1,1-trifluoro-2-chloroethyl radical; pyrolysis; matrix isolation; IR spectroscopy; quantum-chemical calculations.

The interest in products of decomposition of fluorinecontaining compounds is associated with their participation in processes in the troposphere favoring the formation of "ozone holes." Many publications devoted to the study of atmospheric chemical reactions, which postulate the participation of free radicals, have appeared in recent years. The mechanisms of similar reactions are mainly elucidated from the data of kinetic studies and analysis of the stable products that formed.<sup>1-5</sup> The direct IR spectroscopic detection makes it possible to study the reaction mechanisms and obtain information about the structure of intermediates. The existence of the 1,1,1-trifluro2-chloroethyl radical (1) was predicted by the theoretical calculations<sup>6</sup> and assumed upon laser irradiation of  $CF_3CHBrCl^7$  and on the basis of the UV spectra of the products of the reaction of  $CF_3CH_2Cl$  with fluorine atoms;<sup>1</sup> however, IR spectroscopic data on this species were lacking. This work is devoted to the direct IR spectroscopic study of 1,1,1-trifluoro-2-chloroethyl radical formed by the thermolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane (2). We have shown previously that the high-vacuum pyrolysis of bromine- or iodine-containing compounds is accompanied by the formation of free radicals.<sup>8-10</sup>

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#### Experimental

The pyrolysis of compound 2 was carried out at 1150-1300 K and 10<sup>-4</sup> Torr in a quartz 50-120-mm reactor with a diameter of 5 mm attached to an optical helium cryostat. The pyrolysis products were co-deposited along with an excess of argon (~1:1000) on the polished surface of a copper cube cooled to 12 K by a Displex 208R cryogenic system with the closed cycle (Air Products & Chemicals). IR spectra with resolution of 1 cm<sup>-1</sup> were recorded in the wave number range of 4000-400 cm<sup>-1</sup> on a Bruker IFS-113v FT-spectrometer by the beam reflection scheme. The starting chloroethane (2) and stable final products were analyzed on an Incos-50 Finnigan MAT GC-MS spectrometer. Quantumchemical calculations were performed by the GAUSSIAN 94 program<sup>11</sup> using the UHF and B3LYP methods in the 6-311G(d,p) basis set on a Power Challenge supercomputer at the Computer Assistance Desk of the Chemical Research Center of the Division of General and Applied Chemistry of the Russian Academy of Sciences (N. D. Zelinsky Institute of Organic Chemistry of the RAS).

### **Results and Discussion**

The IR spectrum of the products of pyrolysis of 2 contained, along with the absorption bands of the starting compound, several groups of new signals (Fig. 1, a), among which we can distinguish the bands of trifluoroethylene (3) at 3158.2, 1781.0, 1354.7, 1257.7, 1172.4, 924.9, and 753.5  $\text{cm}^{-1.12}$  In addition, the bands at 3118.3, 1353.3, 1237.6, 1147.2, 1129.6, 943.3, 824.7, 654.9, 572.0, and 539.0  $cm^{-1}$  belonging to a labile species were observed. These signals changed simultaneously in intensity when the pyrolysis conditions were varied and disappeared when the matrix was heated to the temperature of diffusion or the pyrolysis products were condensed with additives of 1-5% oxygen. Simultaneously, when the matrix was heated to 35 K, the spectrum exhibited an increase in some bands assigned to hexafluorodichlorobutane (4), which is the formal dimer of 1. The presence of compound 4 in the reaction mixture was confirmed by the GC-MS analysis of the stable products that formed when the matrix was heated to room temperature. Similar results have been reported previously<sup>7</sup> for the products of laser photolysis of 2. This behavior of the bands mentioned above and the presence of the band at 3118.3 cm<sup>-1</sup>, which characterizes the stretching vibration of the C-H bond at the radical center, 13, 14 allowed the bands to be assigned to the unstable species 1,1,1-trifluoro-2-chloroethyl radical (1).

As mentioned above, the ratio of intensities of the IR bands belonging to the primary products of decomposition of chloroethane 2 depends on the pyrolysis conditions. For example, under milder conditions (at a relatively low temperature and a shorter length of the reactor), a higher amount of radical 1 is formed, and the content of ethylene 3 increases as the temperature increases (Scheme 1).

This observation agrees with the assumption that radical 1 is formed by the cleavage of a less stable C-Br



Fig. 1. Comparison of experimental and calculated IR spectra of the 1,1,1-trifluoro-2-chloroethyl radical: *a*, experimental spectrum of products of pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane at T = 1300 K in the 120-mm reactor, *E* are bands of trifluoroethylene, bands of radical 4 are marked with asterisks; *b*, spectrum of radical 1 calculated by the B3LYP method in the 6-311G(d,p) basis set.

#### Scheme 1



bond, whereas the subsequent cleavage of the C–Cl bond requires additional energy expenditure. Unfortunately, we failed to detect the formation of trifluoromethylcarbene, which evidently is isomerized to ethylene 3 already in the pyrolysis zone. Previously,<sup>15</sup> a similar carbene-olefin isomerization has been observed under similar conditions for bistrifluoromethylcarbene formed during pyrolysis of bistrifluoromethyldiazirine. The subsequent detachment of the Br and Cl atoms is also evidenced by the data obtained for the cocondensation of the pyrolysis products and a mixture of Ar and oxygen. In this case, the spectrum contains bands at 1484.0 and 1442.7 cm<sup>-1</sup> assigned to BrOO<sup>-16</sup> and ClOO<sup>-</sup>,<sup>17</sup> respectively, and the band at 1442.7 cm<sup>-1</sup> increased in intensity relative to the band at 1484.0 cm<sup>-1</sup> when the pyrolysis was carried out under a more drastic conditions.

We performed the *ab initio* calculation (see Tables 1 and 2, Fig. 1, *b*) to assign reliably the bands observed in

Approxi-	Experiment		B3LYP/6-311G(d,p) calculation	
mate assignment	∨ /cm <sup>~1</sup>	l <sub>rel</sub>	∨ /cm <sup>-1</sup>	/ /km mol <sup>-1</sup>
v(CH)	3118.3	w	3245.6	3
δ(HCC),	1353.3	m	1354.5	102
$v_s(CF_3)$				
$v_{as}(CF_3)$	1237.6	S	1245.0	169
$v_s(CF_3)$	1147.2	vs	1145.8	245
$v_{as}(CF_3)$	1129.6	٧S	1121.3	323
v(CC),	943.3	m	934.2	94
&(HCC)				
v(C-CI),	824.7	w	818.8	19
δ(HCC)				
$\delta_{c}(CF_{3})$	654.9	w	648.8	22
w(HCCl),	572.0	w	565.0	6
δ.(CF3)				
$\delta_{as}(CF_3)$	539.0	vw	532.1	4
$\delta_{as}(CF_3),$			415.3	3
w(HCCl)				
&(CICC)			365.3	0
$\rho(CF_1)$			243.7	2
$\rho(CF_3)$			183.5	2
τ(CF <sub>3</sub> )			45.0	4

 Table 1. Comparison of experimental and calculated frequencies of the vibrational spectrum of the 1,1,1-trifluoro-2-chloroethyl radical

the IR spectrum to normal vibrations of radical 1 and to refine its structure. The calculations were performed by the UHF methods using the 3-21G, 6-31G(d), and 6-311G(d,p) basis sets and by the B3LYP method using the 6-31G(d) and 6-311G(d,p) basis sets. The best agreement of the calculated and experimental data was achieved when the B3LYP/6-311G(d,p) method was used. In this case, the difference between the calculated and experimental frequencies did not exceed 10 cm<sup>-1</sup>, except for the frequency of the v(C-H) stretching vibration for which this method usually gives overestimated values.<sup>18</sup>

The bands observed in the spectrum were assigned to normal vibrations of radical 1 on the basis of comparison with the published data and visualization of the calculated frequencies and shapes of vibrations by the MolDraw program.<sup>19</sup>

The bands observed in the IR spectrum at frequencies lower than  $1400 \text{ cm}^{-1}$  are noncharacteristic, and the vibrations have a complex character (see Table 1).

Radical 1 has the  $C_1$  symmetry, and all 15 vibrations are active in the IR spectrum. We observed 10 absorption bands that characterize all vibrations possible in the 4000-450 cm<sup>-1</sup> range. As can be seen in Table 1, the calculation method used gave a good agreement of the calculated and experimental values of vibrational frequencies and intensities of the IR bands, which makes it possible to conclude that the data obtained on the radical structure are reliable.

The calculations show that the CHCl fragment is virtually planar. This fact as well as shortening of the

**Table 2.** Calculated bond lengths (d) and angles  $(\omega, \phi)$  of radical 1

1(~)	
	۱
C(1) - C(2) = 0	'
F(3)***/	
C/1)	

E(2)

		<i>e</i> (1)			
Bond	d/À	Bond	d/Å		
C(1)-C(2) 1.487 C(2)-H 1.078 C(1)-F(1) 1.348		C(1)-F(2) C(1)-F(3) C(2)-Cl	1.347 1.354 1.702		
Angle	ω/deg	Angle	φ/deg		
H-C(2)-C(1)-F(1)-C(1)-F(2)-C(1)-F(3)-C(1)-F(3)-C(1)-C(2)-C(1)-C(2)-C(1)-C(2)-C(2)-C(2)-C(2)-C(2)-C(2)-C(2)-C(2	(1) 120.8 ·C(2) 109.1 ·C(2) 112.6 ·C(2) 112.6 ·C(2) 112.6 C(1) 120.2	H-C(2)-C( H-C(2)-C( H-C(2)-C( CI-C(2)-C(	$\begin{array}{rrrr} 1) - F(1) & -18.3 \\ 1) - F(2) & -138.4 \\ 1) - F(3) & 100.9 \\ (1) - F(1) & 172.4 \end{array}$		

Note: ab initio B3LYP/6-311G(d,p) calculation.

C-H bond to 1.078 Å obtained by the calculations (see Table 2) agree well with the high value of the absorption band at 3118.3 cm<sup>-1</sup> observed in the IR spectrum and assigned to the v(C-H) vibration. As have been already mentioned above, the frequency value, which is relatively high for the C-H bond and lies in the narrow 3105-3120 cm<sup>-1</sup> interval, is characteristic of antisymmetrical stretching vibrations of the C-H bond at the terminal radical center and close to that observed previously for alkyl radicals.<sup>14,15</sup>

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# A new hexahydroxysteroid from the Far Eastern starfish Luidiaster dawsoni

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A new polyhydroxysteroid was isolated from the starfish Luidiaster dawsoni; the structure of the product was established as (24S,25R)-24-methylcholestane- $3\beta$ , $5\alpha$ , $6\beta$ , $15\alpha$ , $16\beta$ ,26-hexaol. A mixture of methyl- $\alpha$ - and  $-\beta$ -D-glucopyranosides was also isolated from the extract of this starfish.

Key words: starfish, Luidiaster dawsoni, polyhydroxysteroid.

The starfish, unlike other animals, contains highly oxidized steroids with five to nine hydroxyl groups in a molecule.<sup>1</sup> As a continuation of studies dealing with highly hydroxylated steroid metabolites of the Far Eastern starfish,<sup>2,3</sup> we isolated a new steroid hexaol (1) in a yield of  $9 \cdot 10^{-5}\%$  of the crude animal weight from a methanolic extract of the starfish *Luidiaster dawsoni*. Compound 1 was prepared and purified using successive chromatography on Amberlite XAD-2, Sephadex LH-20, silica gel, and Phlorisil followed by high-performance liquid chromatography (HPLC) on the inverted phase Silasorb C<sub>18</sub>.

The structure of compound 1 was established by <sup>1</sup>H NMR spectroscopy. The arrangement of the hydroxyl groups in the steroid nucleus was determined in spin-decoupling experiments, whose results are presented in Fig. 1. The configurations of substituents were established based on the spin-spin coupling constants of protons (see Experimental). Based on the results obtained, we found that the hydroxyl groups in the steroid nucleus of compound 1 occupy the  $3\beta$ , $5\alpha$ , $6\beta$ , $15\alpha$ , $16\beta$  positions. The structure of the steroid nucleus was confirmed by a comparison of the proton chemical shifts and spin-spin coupling constants in the <sup>1</sup>H NMR spectra (C<sub>5</sub>D<sub>5</sub>N) of hexaol 1 and the polyhydroxysteroids with a similar steroid nucleus that we isolated previously from the *Ctenodiscus crispatus* starfish.<sup>3</sup>



Fig. 1. Arrangement of hydroxyl groups in the steroid nucleus. The arrows show the difference spin decoupling and the dashed arrows correspond to the nuclear Overhauser effect.

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