Mendeleev Commun., 2000, 10(4), 125–126

Photoisomerization of the perfluoroallyl radical: a FTIR matrix-isolation study

Esfir G. Baskir,* Victor A. Korolev and Oleg M. Nefedov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 5328; e-mail: bas@cacr.ioc.ac.ru

10.1070/MC2000v010n04ABEH001318

The perfluoropropen-2-yl radical was found to be the main product of photolysis of the perfluoroallyl radical.

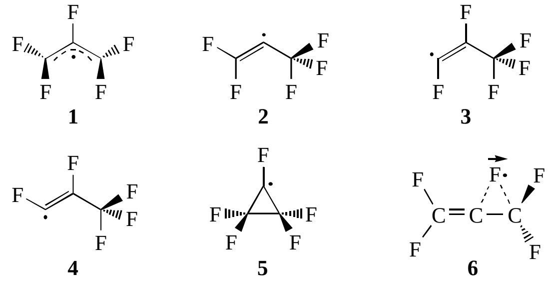
Free radicals are important intermediates in chemical reactions, as well as in atmospheric chemistry, catalysis and biochemistry. Matrix isolation provides an opportunity to detect these transient species and to study their transformations, including photochemical reactions. The allyl radical, which is the simplest conjugated system, is one of the best studied radicals.[1–7] In particular, it was found by matrix IR spectroscopy that photoirradiation of the allyl radical results in both isomerization to the cyclopropyl radical and decomposition to allene or isomeric methylacetylene.[4,5] Data on a perfluorinated analogue of the allyl radical are scanty. Radical C_3F_5 **1** was first obtained photochemically by the interaction of the tributylsilyl radical with 3-bromopentafluoropropene and detected in a cyclopropane solution by EPR spectroscopy.[8] More recently, we measured the matrix IR spectrum of radical **1** generated by pyrolysis of perfluorohexa-1,5-diene.[9] In this work, we examined perfluoroallyl radical **1** and its photoisomerization products in more detail using matrix IR spectroscopy and quantum-chemical calculations.

The experimental procedure was described previously.[10,11] Perfluorohexa-1,5-diene was pyrolysed at 1150–1300 K and a pressure of 10^{-4} Torr in a quartz reactor (50–120 mm in length and 5 mm in diameter) connected to an optical helium cryostat. The pyrolysis products with a high excess of argon (~1 : 1000) were frozen on the polished surface of a copper cube cooled to 10 K by a Displex 208R closed-cycle cryogenic system (Air Products & Chemicals). The IR spectra were recorded on a Bruker IFS-113v Fourier-transform spectrometer with a resolution of 0.5 cm^{-1} in the frequency range 4000–400 cm^{-1} using the beam reflection scheme. The photolysis was carried out with a high-pressure mercury lamp (1000 W), and the irradiation wavelength was varied using glass filters.

The UV irradiation ($260 < \lambda < 400$ nm) of an Ar matrix containing the pyrolysis products resulted in a synchronous decrease in the intensities of the IR bands belonging to radical **1** (Table 1, Figure 1). The intensities of some bands, among which were the absorption bands of perfluoroallene (2065.1, 1284.2, 1238.8, 1033.4 and 609.0 cm^{-1})[12] and isomeric perfluoromethylacetylene (1373.8, 1164.8, 1102.6 and 766.2 cm^{-1}),[13] increased simultaneously. New bands at 1785.4, 1307.8, 1262.0, 1166.4, 1149.1, 1009.3, 698.3, 598.5 and 530.8 cm^{-1} were of special interest. The appearance of these bands was not associated with transformations of the starting perfluorohexa-1,5-diene, which was present in the mixture of pyrolysis products, because the intensities of its IR absorption bands remained unchanged after irradiation of the matrix. Moreover, a control experiment on the photolysis of the starting compound specially sputtered in the matrix also showed no changes in the spectrum. The absorption band intensities of pyrolysis by-products such as the CF_3 radical and perfluoropropylene CF_3CFCF_2 did not decrease. Thus, the new bands can be attributed to the products of phototransformation of only radical **1**.

The heating of the matrix to a diffusion temperature (35 K) was accompanied by a decrease in the intensity of these bands and by the simultaneous appearance and growth of several IR bands (1743.3, 1380,8, 1221.8, 1131.6, 1110.0, 1045.3, 996.6 and 741.6 cm^{-1}) belonging to stable molecules. Hence it follows that the new IR bands belong to an unstable species, whereas the bands appeared during the heating probably belong to recombination products. Moreover, the IR bands of the photoproduct **1** did not coincide with the bands of the known intermediates that can be formed in the decomposition of **1**, namely, $CF_2{=}CF$[14] and CF_3[15] radicals or difluorocarbene CF_2.[15] Therefore, the photoproduct from **1** is most likely a photoisomer of this species.

To reveal the structure of the species formed, we compared the experimental data with the results of quantum-chemical calculations. The optimum geometry and vibrational spectrum were calculated by both the classical *ab initio* UHF method in the 3-21G, 6-31G and 6-311G* basis sets and the B3LYP density functional method (DFT) in the 6-311G* basis set using the GAUSSIAN-94 program system.[16] Perfluoroallyl radical **1** was chosen as a model for the determination of the most appropriate calculation method. In the calculations of radical **1**, the B3LYP method with the 6-311G* basis set gave the most plausible results, which showed the presence of aligned C–C bonds and a somewhat nonplanar geometry (symmetry C_2). This method also gave the best agreement between the experimental and calculated signals in both frequency (the average deviation did not exceed 2%) and intensity. A comparison between the calculated and experimental spectra of radical **1** allowed us to detect previously unobserved IR bands and to assign more adequately the IR bands to normal vibrations. According to this calculation, an intense absorption band at 1499.3 cm^{-1} corresponds to the antisymmetric stretching vibration of C–C, confirming electron delocalization in the allylic system of radical **1**. The experience gained from the calculation of radical **1** was used in the consideration of isomeric structures. Five different isomers are plausible for a species with the molecular formula C_3F_5 (Scheme 1). We calculated the structures, energy parameters and vibrational spectra of these isomers by the B3LYP method in the 6-311G* basis set.



Scheme 1

The stability of these species was found to decrease in the following order: allylic structure **1** > propen-2-yl **2** > *trans*- and *cis*-propen-1-yl radicals **3**, **4** > cyclopropyl radical **5** (Table 1).

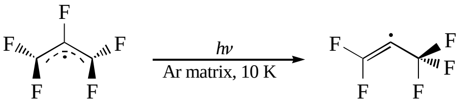
The photoisomerization of the allyl radical can proceed with the formation of a cyclopropyl structure.[4,5] However, the experimental set of IR bands of the photoisomer was strongly different from that predicted by the quantum-chemical calculation for analogous perfluorinated species **5** (Table 1). Because the spectrum of the photolysis products exhibits a band at 1875.4 cm^{-1}, which is characteristic of polyfluoroalkenes and indicates the presence of the C=C bond in the molecule, structures **2**–**4** can be attributed to the photoisomer. In our case, the best agreement between the experimental and calculated frequencies of the vibrational spectrum was observed for the structure of radical **2**

Table 1 Experimental and calculated (B3LYP/6-311G*) vibrational frequencies (ν) in the range 4000–400 cm^{-1}, total (E) and relative (ΔE) energies of the perfluoroallyl radical and its isomers.

ν/cm^{-1}			ν/cm^{-1}					
Calculated[a]	Experimental	Assignment	Calculated[a]				Experimental	Assignment
1			**5**	**3**	**4**	**2**		
1596.5 (5)		ν_s(C–C)	1515.0 (20)	1784.1 (40)	1790.0 (116)	1838.8 (419)	1785.4 s	ν(C=C)
1531.7 (262)	1499.3 s	ν_{as}(C–C)	1272.7 (111)	1341.0 (141)	1363.9 (133)	1303.5 (101)	1307.8 m	ν_s(CF$_2$), ν(C–C)
1360.6 (311)	1350.9 s	ν_{as}(CF$_2$)	1216.3 (461)	1238.7 (390)	1230.0 (46)	1253.3 (382)	1262.0 vs	ν_{as}(CF$_2$)
1305.8 (46)	1301.2 w	ν_{as}(CF$_2$)	1205.8 (266)	1198.9 (198)	1181.9 (434)	1156.1 (333)	1166.4 s	ν_{as}(CF$_3$),
1212.4 (191)	1215.1 s	ν(CF)	1177.2 (48)	1158.9 (305)	1159.5 (309)	1126.9 (230)	1149.1 m	ν_{as}(CF$_3$), ν(C–C)
1009.6 (269)	1007.7 s	ν_s(CF$_2$), ν_s(C–C)	856.7 (123)	1106.4 (195)	1067.5 (263)	1010.8 (305)	1009.3 m	ν_s(CF$_2$), ν_s(CF$_3$)
729.7 (0)		ν_s(CF$_2$), δ_s(CF$_2$)	819.2 (39)	778.9 (2)	843.6 (12)	808.4 (5)		δ(CCC), ν_s(CF$_2$)
575.4 (2)	581.2 vw	δ_{as}(CF$_2$)	760.9 (4)	636.7 (0)	718.2 (26)	688.9 (14)	698.3 w	δ_s(CF$_3$), δ(CCC)
572.2 (0)		ρ_r(CF$_2$)	750.6 (1)	625.6 (2)	637.1 (0)	633.0 (17)		ρ_r(CF$_2$)
451.4 (12)		ρ_w(CF)	568.3 (1)	575.9 (13)	577.6 (1)	599.1 (7)	598.5 w	δ_s(CF$_2$), δ_s(CF$_3$)
397.7 (4)		ρ_w(CF$_2$)	541.9 (15)	513.1 (6)	494.1 (2)	577.9 (0)		δ_{as}(CF$_3$), ρ_w(CF$_2$)
381.1 (1)		ρ_r(CF$_2$)	439.6 (3)	484.7 (2)	408.7 (1)	523.5 (3)	530.8 vw	ρ_r(CF$_3$)
E (hartrees)	–613.5879		–613.5386	–613.5692	–613.5707	–613.5828		
ΔE/kJ mol^{-1}			12.9	4.9	4.5	1.3		

[a] Calculated intensities in km mol^{-1} are given in parentheses.

(Table 1), whose formation can be explained by the 1,2-migration of a fluorine atom in radical **1** (Scheme 2).



1 **2**

Scheme 2

The potential barrier for this process calculated by the B3LYP/6-311G* method is equal to 18.1 kJ mol^{-1}. Transition state **6** corresponding to the fluorine transfer from the allylic position to a terminal carbon atom is characterised by a negative frequency (–234 cm^{-1}) related to the migration of a fluorine atom between the adjacent carbon atoms. Indeed, the calculation of the energy along the internal reaction coordinate (IRC) confirmed that **6** is a transition state, and a shift to one or another side along the potential-energy curve results in one of the two minima corresponding to the structures of **1** and **2**. Moreover, the bands at 1307.8, 1262.0, 1166.4 and 1149.1 cm^{-1} attributed to radical **2** can also be observed as weak absorption bands in the spectrum of the primary products of pyrolysis along with the intense IR bands of radical **1**. In fact, according to the quantum-chemical calculation, the difference between the energies of formation of radicals **1** and **2** is approximately equal to 1.3 kJ mol^{-1} in favour of **1**, and its formation under conditions of high-temperature pyrolysis is the main process, whereas the concentration of **2** in the equilibrium mixture can be as high as several percent.

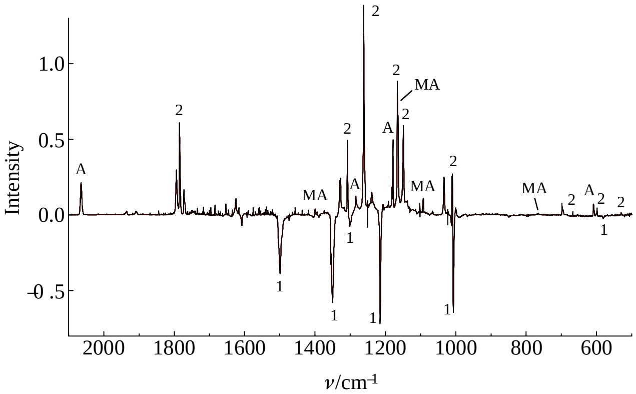


Figure 1 Difference IR spectrum of the products of pyrolysis of 1,5-perfluorohexadiene in an argon matrix at 10 K before photolysis (bands directed down: 1 is the perfluoroallyl radical) and after photolysis (bands directed up: 2 is the perfluoropropen-2-yl radical, MA is perfluoromethylacetylene and A is perfluoroallene).

Thus, the photolysis of perfluoroallyl radical **1** isolated in an argon matrix results in the formation of a new unstable species, which was identified as perfluoropropen-2-yl radical **2** on the basis of the data of matrix IR spectroscopy and quantum-chemical calculations.

This work was supported by the Russian Foundation for Basic Research (grant nos. 98-07-90290, 99-15-78323 and 97-03-33740) and INTAS (grant no. 96-0866).

References

1 A. K. Maltsev, V. A. Korolev and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 555 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 510).

2 E. Vajda, J. Tremmel, B. Rozsondai, I. Hargittai, A. K. Maltsev, N. D. Kagramanov and O. M. Nefedov, *J. Am. Chem. Soc.*, 1986, **108**, 4352.

3 R. Glaser and G.-C. Choy, *J. Phys. Chem.*, 1994, **98**, 11379.

4 K. Holtzhauer, C. Cometta-Morini and J. F. M. Oth, *J. Phys. Org. Chem.*, 1990, **3**, 219.

5 G. Maier and S. Senger, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 558.

6 D. Uy, S. Davis and D. J. Nesbitt, *J. Chem. Phys.*, 1998, **109**, 7793 and references therein.

7 D. Stranges, M. Stemmler, X. Yang, J. D. Chesko, A. G. Suits and Y. T. Lee, *J. Chem. Phys.*, 1998, **109**, 5372.

8 B. E. Smart, F. J. Krusic, F. Meakin and R. C. Bingham, *J. Am. Chem. Soc.*, 1974, **96**, 7382.

9 A. K. Maltsev, E. G. Baskir, N. D. Kagramanov and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1998 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1817).

10 V. A. Korolev and E. G. Baskir, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 464 (*Russ. Chem. Bull.*, 1995, **44**, 448).

11 E. G. Baskir and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 109 (*Russ. Chem. Bull.*, 1996, **45**, 99).

12 J. R. Durig, Y. S. Li, J. D. Witt, A. P. Zens and P. D. Ellis, *Spectrochim. Acta*, 1977, **33A**, 529.

13 W. Stuckey and J. Heicklen, *J. Am. Chem. Soc.*, 1968, **90**, 3952.

14 A. Thoma, B. E. Wurfel, R. Schlachta, G. M. Lask and V. E. Bondybey, *J. Phys. Chem.*, 1992, **96**, 7231.

15 D. E. Milligan and M. E. Jacox, *J. Phys. Chem.*, 1968, **48**, 2265.

16 J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94, Revision D.1*, Gaussian, Inc., Pittsburgh PA, 1995.

Received: 25th April 2000; Com. 00/1644