Journal of Fluorine Chemistry, 37 (1987) 47–51

Received: January 16, 1987; accepted: March 25, 1987

THE INFRARED SPECTRA OF GASEOUS 1,1,3,3-TETRACHLOROTETRAFLUORO-4-(TRIFLUOROMETHYLDIOXY)BUTYL TRIFLUOROMETHYL ETHER AND 1,1,3,3-TETRACHLOROTETRAFLUORO-1,4-BIS(TRIFLUOROMETHOXY)BUTANE

JUANA CZARNOWSKI

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA)*, Casilla de Correo 16, Sucursal 4, (1900) La Plata, Argentina

SUMMARY

1,1,3,3-Tetrachlorotetrafluoro-4-(trifluoromethyldioxy)butyl trifluoromethyl ether, $CF_3O(CF_2CCl_2)_2O_2CF_3$, was formed as one of the products in the reaction of $CF_3O_3CF_3$ with CF_2CCl_2 at 322.6 - 342.5 K. It was isolated by fractional condensation between 213 and 243 K and characterized by molecular weight determination and ^{19}F NMR spectrum. 1,1,3,3-Tetrachlorotetrafluoro-1,4-bis(trifluoromethoxy)butane, $CF_3O(CF_2CCl_2)_2OCF_3$, was condensed as residue at 193 K from the reaction of CF_3OF with CF_2CCl_2 at 266 - 302.7 K, when $[CF_2CCl_2]/[CF_3OF] \leq 0.5$. It was characterized by gas chromatography and molecular weight determination. The infrared spectra of both compounds are given, providing additional support for their characterization.

RESULTS AND DISCUSSION

The gaseous infrared spectra of 1,1,3,3-tetrachlorotetrafluoro-4-(trifluoromethyldioxy)butyl trifluoromethyl ether, $CF_3O(CF_2CCl_2)_2O_2CF_3$, and 1,1,3,3-tetrachlorotetrafluoro-1,4-bis(trifluoromethoxy)butane, $CF_3O(CF_2CCl_2)_2OCF_3$, have been recorded in connection with kinetic and mechanistic studies of the respective reactions of 1,1-dichlorodifluoroethylene, CF_2CCl_2, with

* Facultad de Ciencias Exactas, Universidad Nacional de La Plata.

0022-1139/87/$3.50

$CF_3O_3CF_3$ and CF_3OF [1,2]. The infrared spectra of both compounds are illustrated in Fig. 1 and 2 respectively. Their comparison is presented in Table 1. They have not been previously reported.

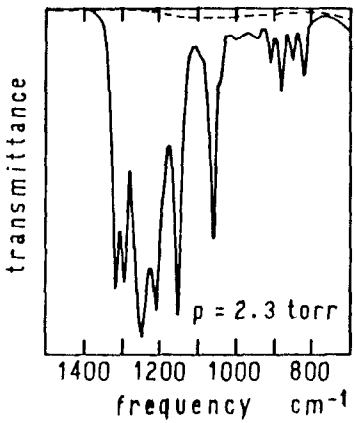

Fig. 1. The infrared spectrum of $CF_3O(CF_2CCl_2)_2O_2CF_3$.

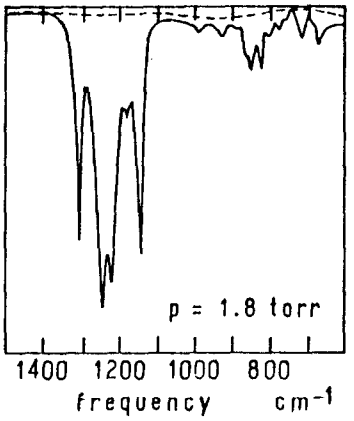

Fig. 2. The infrared spectrum of $CF_3O(CF_2CCl_2)_2OCF_3$.

The infrared spectra were recorded on a Perkin-Elmer 221 spectrometer, using 10 cm gas cell with sodium chloride windows.

The chromatograms were recorded on a Gow-Mac 625 gas chromatograph, provided with gas density detector. The column was of 4% SE-30 on acid washed chromosorb W.

The ^{19}F NMR spectra were taken with a Varian EM360L spectrometer, using $CFCl_3$ as internal reference.

Preparation and identification of $CF_3O(CF_2CCl_2)_2O_2CF_3$

This compound was obtained as one of the four products of the gas-phase reaction of $CF_3O_3CF_3$ with CF_2CCl_2 [1]. The initial pressure of $CF_3O_3CF_3$ was varied between 7 and 240 torr and that of CF_2CCl_2 between 4 and 600 torr. Fifty experiments were made between 322.6 and 342.5 K.

The reactants were removed from the reaction system at 183 K leaving the products as residue.

The products of 40 experiments were collected together and separated by fractional condensation at 213, 243 and 268 K in four fractions. Their quantitative ^{19}F NMR spectra provided

strong evidence that each fraction consisted of $CF_3O(CF_2CCl_2)O_2CF_3$, $CF_3O(CF_2CCl_2)_2O_2CF_3$, $CF_3O(CF_2CCl_2)_3O_2CF_3$ and $CF_3O(CF_2CCl_2)_4O_2CF_3$ respectively. The spectra presented the characteristic line (68.1 ppm) due to CF_3OO as well as the CF_3O line (56.8 ppm) [3].

The infrared spectrum of the fraction separated between 213 and 243 K corresponding to $CF_3O(CF_2CCl_2)_2O_2O_2CF_3$ was compared with that of $CF_3O(CF_2CFCl)_2O_2CF_3$ [3]. In both spectra the bands of CF_3O and CF_3OO groups appeared at almost the same wave lengths.

Additional support to identification of this fraction was given by its molecular weight determination by gas-density measurements with a calibrated Pyrex bulb. The value of $456^{\pm}9$ was obtained. The theoretical molecular weight of $CF_3O(CF_2CCl_2)_2O_2CF_3$ is 452.

The infrared spectra of all fractions were similar, as expected for compounds belonging to an homologous series [4].

Preparation and identification of $CF_3O(CF_2CCl_2)_2OCF_3$

This compound was one of the gaseous products of the reaction of CF_3OF with CF_2CCl_2 [2], studied between 266 and 302.7 K. The ratio of the initial concentration of CF_2CCl_2 to that of CF_3OF, $R_i = [CF_2CCl_2]_i/[CF_3OF]_i$, varied between 17.2 and 0.03.

CF_3OF was removed from the reaction mixture at 128 K. The products CF_3CFCl_2 and $CF_3O(CF_2CCl_2)F$ were separated together with CF_2CCl_2 as volatiles at 193 K and identified by their infrared spectra [5,6].

Gas chromatograms of the residue of different experiments left at 193 K were recorded. If $R_i \leq 0.5$ only one peak appeared, indicating that in these conditions the residue consisted of one compound only. The comparison of its infrared spectrum with that of $CF_3O(CF_2CFCl)_2OCF_3$ [3] permits tentatively recognize this compound as $CF_3O(CF_2CCl_2)_2OCF_3$.

As additional evidence the molecular weight of this compound has been determined by gas-density measurements using a calibrated Pyrex bulb. The value obtained was $433^{\pm}7$. The theoretical molecular weight of $CF_3O(CF_2CCl_2)_2OCF_3$ is 436.

Increasing R_i the number of peaks on the chromatograms increased. If $R_i > 9$, in addition to gaseous products a small amount of non-volatile liquid was formed. Plotting log of the

TABLE 1

The comparison of the infrared spectra of gaseous $CF_3O(CF_2CCl_2)_2O_2CF_3$ and $CF_3O(CF_2CCl_2)_2OCF_3$.

$CF_3O(CF_2CCl_2)_2O_2CF_3$	$CF_3O(CF_2CCl_2)_2OCF_3$	Tentative
Frequency cm^{-1} (a)	Frequency cm^{-1} (a)	Assignment
1314 (vs)	1306 (vs)	
1292 (vs)		
1245 (vvs)	1242 (vvs)	CF_3
1206 (vs)	1218 (vs)	
	1171 (m)	
1148 (vs)	1148 (vs)	
1082 (m)	1055 (w)	CF_2
1055 (s)		
987 (m)	970 (m)	
947 (m)	954 (w)	C-C
936 (m)		
902 (s)	911 (m)	
875 (s)	880 (m)	
842 (s)	839 (s)	
814 (s)	812 (s)	
	789 (m)	CCl_2
	765 (m)	
	746 (w)	
706 (m)	706 (s)	
663 (m)	660 (s)	

(a) s-strong, m-medium, w-weak, v-very.

retention time vs. the ordinal number of the respective peak straight lines were obtained proving that the products were members of an homologous series [7].

ACKNOWLEDGEMENTS

The author wishes to thank Dr. A.L. Capparelli for having carried out the nuclear magnetic resonance measurements. This work was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

REFERENCES

1 J. Czarnowski, Int.J.Chem.Kinet., 18 (1986) 1323.
2 M. dos Santos Afonso and J. Czarnowski, submitted for publication.
3 F.A. Hohorst, J.V. Paukstelis and D.D. DesMarteau, J.Org.Chem., 39 (1974) 1298.
4 R.N. Haszeldine and B.R. Steele, J.Chem.Soc., (1953) 1592.
5 J.R. Nielsen, C.Y. Liang, R.M. Smith and D.C. Smith, J.Chem. Phys., 21 (1953) 383.
6 K.K. Johri and D.D. DesMarteau, J.Org.Chem., 48 (1983) 242.
7 H.M. McNair and E.J. Bonelli, 'Basic Gas Chromatography', Berkeley, Consolidated Printers (1968).