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Journal of Fluorine Chemistry 74 (1995) 199–201

JOURNAL OF FLUORINE CHEMISTRY

The thermal addition of trifluoromethyl hypofluorite, CF_3OF, to tetrachloroethene

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Received 15 November 1994; accepted 18 March 1995

Abstract

The trifluoromethyl 1,1,2,2-tetrachloro-2-fluoroethyl ether, $CF_3OCCl_2CCl_2F$, was the major product of the thermal gas-phase reaction of CF_3OF with tetrachloroethene at 313.8–343.8 K. Other products were CCl_2FCCl_2F and $CF_3O(CCl_2CCl_2)_2OCF_3$. The yields of the ether, based on the sum of the products, increased from 97.7% to 99.5% when the initial ratio of CF_3OF to that of CCl_2CCl_2 increased from 1.075 to 10.08. The IR spectrum of $CF_3OCCl_2CCl_2F$ is given.

Keywords: Thermal addition; Trifluoromethyl hypofluorite; Tetrachloroethene; IR spectroscopy

1. Introduction

The trifluoromethyl hydrohaloethyl ethers and the trifluoromethyl haloethyl ethers are the major products of the addition of CF_3OF to the corresponding parent alkenes [1–3].

In this work, characterization of the products of the thermal gas-phase addition of CF_3OF to tetrachloroethene, not reported previously, has been undertaken.

2. Experimental details

The reaction proceeded with a pressure decrease. The experiments were done in a grease-free static system. A spherical quartz bulb of 270 cm^3 volume was used as a reaction vessel. It was connected to the vacuum line and to the storage traps containing reactants condensed at liquid-air temperature. The reaction vessel temperature was maintained to within ± 0.1 K using a Lauda thermostat. To charge the reactants, the storage traps were heated up to the desired temperatures, and the gaseous reactants introduced into the evacuated reaction vessel. The pressure was measured with a quartz spiral gauge. CF_3OF was always introduced last and in excess.

Infrared spectra were recorded on a Perkin-Elmer spectrometer, using a 10 cm cell with NaCl windows. Chromatograms were performed on a Gow-Mac gas chromatograph, using a column containing 5% SE-30 on Chromosorb W-AW at 273 K. The carrier gas was N_2. This chromatograph is provided with a gas density balance detector, which allows the determination of the relative molecular mass of an unknown compound X using the formula: $M_X = KA_X/PV + M_c$ [4], where M_c is the relative molecular mass of the carrier gas, P and V are the pressure and volume of the gas X, K is the constant of the chromatograph determined for pure CF_3OF and A_X is the peak area of the compound X. The percentage composition of a gas mixture can be calculated by multiplying each peak area by $F_j = M_j/(M_j - M_c)$, where M_j is the relative molecular mass of each component, and then dividing each corrected area by the sum of all corrected areas.

3. Results and discussion

Thirty-four experiments were made in the temperature range 313.8–343.8 K. The initial pressure of CF_3OF was varied between 10.8 and 77.5 Torr and that of CCl_2CCl_2 between 3.7 and 26.8 Torr. The initial ratio of CF_3OF to that of CCl_2CCl_2 increased from 1.075 to 10.08.

All experiments led to complete consumption of CCl_2CCl_2. In order to analyze the reaction mixture of each experiment, the reaction vessel was rapidly cooled to liquid-air temperature. CF_3OF was eliminated as a volatile by fractional condensation at 153 K. The residual fraction was divided into

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SSDI 0022-1139(95)03276-2

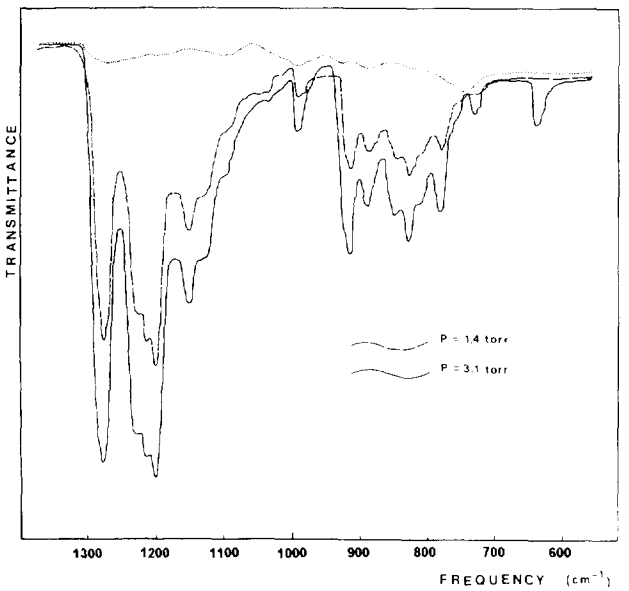

Fig. 1. Infrared spectrum of $CF_3OCCl_2CCl_2F$.

Table 1
Infrared spectrum of $CF_3O(CCl_2CCl_2)F$

Frequency (cm^{-1}) [a]	Tentative assignment	Frequency (cm^{-1}) [a]	Tentative assignment
1276 (vvs)	CF_3	912 (s)	C–Cl
1228 (vs)	CF_3	885 (s)	C–Cl
1210 (vvs)	CF_3	844 (s)	C–Cl
1196 (vvs)	CF_3	824 (s)	C–Cl
		805 (s)	C–Cl
1148 (s)	C–F	777 (s)	C–Cl
1124 (s)	C–F	728 (w)	C–Cl
		634 (w)	C–Cl
988 (m)	C–O		

[a] v = very, s = strong; m = medium; w = weak .

samples I and II. Chromatograms of each sample I were performed. Three peaks P_1, P_2 and P_3 always appeared. Their retention times were different from that of CCl_2CCl_2. The corresponding areas were $A_2 \gg A_1 \approx A_3$, where the subscript denotes the ordinal number of each peak.

Samples II derived from successive experiments were condensed together. The condensate obtained was separated by fractional condensation at 223 and 238 K into fractions F_1, F_2 and F_3.

Chromatograms of fraction F_1 exhibited two peaks P_1 and P_2. One of the two compounds was identified by its IR spectrum as CCl_2FCCl_2F [5].

In chromatograms of fraction F_2 only one peak, P_2, appeared. The corresponding compound was characterized as $CF_3OCCl_2CCl_2F$ by chromatographic determination of the relative molecular mass of fraction F_2. The value obtained was 265 ± 21. The theoretical value for the relative molecular mass of $CF_3OCCl_2CCl_2F$ is 270.

The infrared spectrum of $CF_3OCCl_2CCl_2F$ is illustrated in Fig. 1. The corresponding band frequencies are listed in Table 1. These frequencies indicate the presence of the structural groups CF_3, C–F, C–O and C–Cl. The strong absorption bands at 1280–1180 cm^{-1}, due to the CF_3O group, are characteristic of compounds such as $CF_3O(E)F$, where E = alkene [1].

Two peaks, P_2 and P_3, appeared in chromatograms of fraction F_3. The gas density balance detector allows determination of the relative molecular mass of an unknown compound of a gaseous mixture [4] using the formula $M_3 = (KA_3 + f_3PVM_c)/f_3PV$, where P and V are the pressure and volume of the gaseous mixture, K is the constant of the chromatograph, A_3 is the peak area of the compound and f_3 is its mole fraction. A value of 496 ± 29 was obtained for M_3, characterizing the compound as $CF_3O(CCl_2CCl_2)_2OCF_3$. Its theoretical relative molecular mass is 502.

The IR spectrum of this fraction is consistent with the proposed structure. It shows bands at 1274 (s); 1230 (s); 1197 (vvs); 1106 (s); 1009 (m); 913 (vs); 885 (m); 855 (vs); 806 (vvs); 776 (m); 728 (vs) cm^{-1}. The strong absorption bands at 1274–1197 cm^{-1} are characteristic of the CF_3O group and the strong absorption bands at 913–728 cm^{-1} are characteristic of the CCl_2 group.

Within the reactants pressure used in this work, only CCl_2FCCl_2F, $CF_3OCCl_2CCl_2F$ and $CF_3O(CCl_2CCl_2)_2OCF_3$ were formed in detectable amounts. The yields of $CF_3OCCl_2CCl_2F$, based on the sum of the products, were calculated from the chromatographic peak areas of the samples I and are summarized in Table 2, where Δt is the reaction time in minutes. The yields of different $CF_3O(E)F$ reported in the literature [1–3] are in the range 75%–100% for stoichiometric concentrations of CF_3OF and parent alkene.

Table 2
Yields of $CF_3OCCl_2CCl_2F$ based on the sum of the products

Run No.	Temp. (K)	Δt (min)	Initial pressure of CF_3OF (Torr)	Initial pressure of CCl_2CCl_2 (Torr)	Yield of $CF_3OCCl_2CCl_2F$ (%)
7	313.8	906.4	17.3	9.8	98.5
3	313.8	420.6	35.8	15.0	98.8
1	313.8	368.8	37.3	11.8	99.0
4	313.8	183.1	55.0	13.3	99.2
6	313.8	243.0	78.2	13.7	99.3
8	313.8	241.7	38.1	4.0	99.5
14	323.8	1218.0	28.8	26.8	97.7
12	323.8	1289.0	16.2	12.7	98.0
9	323.8	277.0	34.2	12.5	98.9
10	323.8	186.4	77.5	14.1	99.2
11	323.8	181.4	37.3	3.7	99.5
20	333.7	1174.0	20.4	15.1	98.2
17	333.7	184.8	39.2	14.1	98.8
19	333.7	158.3	60.3	12.1	99.2
18	333.7	129.4	38.9	5.1	99.3
24	343.8	242.4	11.0	5.6	98.6
22	343.8	152.0	20.5	9.0	98.8
23	343.8	153.4	21.3	4.9	99.1

Acknowledgements

The authors thank Mr. Z. Czarnowski for very helpful comments. This work was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas.

References

[1] K.K. Johri and D.D. DesMarteau, *J. Org. Chem.*, *48* (1983) 242.
[2] A. Sekiya and K. Ueda, *Chem. Lett.*, (1990) 609.
[3] H. Di Loreto and J. Czarnowski, *J. Fluorine Chem.*, *66* (1994) 1.
[4] C.S.G. Phillips and P.L. Timms, *J. Chromatogr.*, *5* (1961) 131.
[5] R.E. Kagarise and L.W. Daasch, *J. Chem. Phys.*, *23* (1955) 113.