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Preliminary Note

The thermal addition of trifluoromethylhypofluorite, CF_3OF, to trichloroethene

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Abstract

The major product of the thermal gas-phase addition of CF_3OF to trichloroethene at 303.8 K was $CF_3O(CHClCCl_2)F$. Other products, i.e. $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)_{n\geq 2}$-$OCF_3$, were formed in minor amounts. A reaction mechanism is proposed.

The major product of the thermal gas-phase reaction of trifluoromethylhypofluorite with trichloroethene is the 1:1 adduct of CF_3OF and $CHClCCl_2$, as indicated by determination of its relative molecular mass. This adduct has been assigned the structure $CF_3OCHClCCl_2F$, following the pattern of addition of CF_3OF to ethenes previously reported in the literature [1, 2], and as illustrated in Table 1 by the yields of the corresponding products. The IR spectrum of the adduct is consistent with the proposed structure. A less abundant product of the reaction has been characterized by determination of its relative mass as $CHClFCCl_2F$, consistent with its IR spectrum. A mixture of less volatile products contained compounds of the type: $CF_3O(CHClCCl_2)_nOCF_3$, where $n=2$–n.

TABLE 1. Reported reactions of CF_3OF with some ethenes

Ethene	Product	Relative amount[a] (%)	Ref.
$CH_2{=}CHBr$	CF_3OCH_2CHBrF	100	1
$CH_2{=}CCl_2$	$CF_3OCH_2CCl_2F$	100	1
$CH_2{=}CF_2$	$CF_3OCH_2CF_3$	97.5–100	1, 2
	$CF_3OCF_2CH_2F$	2	1
	CF_3CH_2F	trace	1
$CH_2{=}CHF$	$CF_3OCH_2CHF_2$	87–90	1, 2
	$CF_3OCHFCH_2F$	13–10	1, 2
$CF_2{=}CCl_2$	$CF_3OCF_2CCl_2F$	63	1
	$CF_3OCCl_2CF_3$	12	1
	CF_3CCl_2F	25	1

[a] Determined by ^{19}F NMR spectroscopy.

To account for the formation of these products, the following radical mechanism has been proposed:

$$CF_3OF + CHClCCl_2 \longrightarrow CHClFCCl_2\cdot + CF_3O\cdot \tag{1}$$

$$CHClFCCl_2\cdot + CF_3OF \longrightarrow CHClFCCl_2F + CF_3O\cdot \tag{2}$$

$$CF_3O\cdot + CHClCCl_2 \longrightarrow CF_3O(CHClCCl_2)\cdot \tag{3}$$

$$CF_3O(CHClCCl_2)\cdot + CF_3OF \longrightarrow \mathit{CF_3O(CHClCCl_2)F} + CF_3O\cdot \tag{4}$$

$$CF_3O(CHClCCl_2)_2\cdot \tag{5}$$

$$CF_3O(CHClCCl_2)_2\cdot + CHClCCl_2 \longrightarrow CF_3O(CHClCCl_2)_3\cdot \tag{6}$$

$$CF_3O(CHClCCl_2)_i\cdot + CF_3O(CHClCCl_2)_j\cdot \longrightarrow CF_3O(CHClCCl_2)_{i+j}OCF_3 \tag{7}$$

(where $i, j \geqslant 1$ and $i+j=n$)

$$CHClFCCl_2\cdot + CHClCCl_2 = CHClFCCl_2(CHClCCl_2)\cdot \tag{8}$$

$$CHClFCCl_2(CHClCCl_2)\cdot + CHClCCl_2 = CHClFCCl_2(CHClCCl_2)_2\cdot \tag{9}$$

$$CHClFCCl_2(CHClCCl_2)_2\cdot + CHClCCl_2 = CHClFCCl_2(CHClCCl_2)_3\cdot \tag{10}$$

$$CHClFCCl_2(CHClCCl_2)_i\cdot + CHClFCCl_2(CHClCCl_2)_j\cdot = (CHClFCCl_2)_2(CHClCCl_2)_{i+j} \tag{11}$$

(where $i, j \geqslant 1$ and $i+j=n$)

This mechanism is proposed on the basis of free-radical mechanisms postulated in previous kinetic

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studies of the analogous additions of CF_3OF to hexafluoropropene [3], perfluorobut-2-ene [4] and 1,1-dichlorodifluoroethene [5].

The conclusion, drawn by DesMarteau from a study of the additions of CF_3OF to some simple alkenes, is that the reaction products are most readily accounted for on the basis of a free-radical reaction mechanism, consistent with the observed reactivity, regioselectivity and low stereoselectivity [1]. The observed telomerization provides further support for the free-radical reaction mechanism.

The lack of formation of CF_3OOCF_3 corroborates the conclusions of earlier work [5–9] that the addition of $CF_3O\cdot$ to the double bond of alkenes is considerably faster than any other reaction of $CF_3O\cdot$ radicals.

No products of reaction (11) were detected, indicating that relative to other products only very small amounts of these compounds were formed, probably due to the fast removal of $CHClFCCl_2\cdot$ radicals by CF_3OF. The formation of $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)F$ corroborates the results of earlier work [10, 11], indicating that CF_3OF is a successful scavenger for free radicals with which it reacts by fluorine-atom transfer to form the corresponding stable fluoro analogues.

The conversion of $CHClCCl_2$ to $CHCl_2C(O)Cl$ in the presence of CF_3OF and molecular O_2 indicates the free-radical-initiated oxidation of $CHClCCl_2$ [12]. The reported main product of the oxidation of CF_2CCl_2 in the presence of CF_3OF is $CF_2ClC(O)Cl$ [6].

Experimental

The reaction was accompanied by a pressure decrease. Experiments were performed in a grease-free static system allowing pressure measurements at constant volume and temperature. A spherical quartz bulb of 180 cm^3 volume was used as a reaction vessel, connected to the vacuum line and storage traps with the reactants condensed at liquid-air temperature. The temperature of the reaction vessel was maintained to ±0.1 K by means of a Lauda thermostat. To charge the reactants, the traps were heated up to the desired temperature, and the gaseous reactants introduced into the evacuated reaction vessel, with the pressure being measured with a quartz spiral gauge. The reactant in excess was always introduced last.

Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer, using a 10-cm cell with NaCl windows. Chromatograms were performed on a Gow–Mac 625 gas chromatograph, using a 5% SE-30 on Chromosorb W-AW 60–80 mesh (250–177 μm) column of 1.8 m length. Nitrogen was used as the carrier gas. The chromatograph employed was provided with a gas density balance detector, permitting the relative molecular mass of an unknown compound X to be obtained via the formula $M_x = KA_x/PV + M_c$ [13], 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 a constant for the chromatograph determined using pure CF_3OF and A_x is the peak area of compound X.

Experiments were made at 303.8 K, varying the initial pressure of CF_3OF between 7 and 42 Torr and that of $CHClCCl_2$ between 7.9 and 58.5 Torr.

For analysing the reaction mixture of each experiment, the reaction vessel was rapidly cooled to liquid-air temperature and the mixture separated by fractional condensation at 153, 193 and 243 K. CF_3OF was separated as a volatile material at 153 K. The volatile fraction at 193 K consisted of a compound believed to be $CHClFCCl_2F$, as suggested by comparing its infrared spectrum with that of CCl_2FCCl_2F [14]. Unreacted $CHClCCl_2$ and an unidentified compound were separated as volatiles at 243 K.

The infrared spectrum of the volatile fraction at 243 K, obtained from experiments undertaken in the presence of excess CF_3OF, and allowed to proceed to

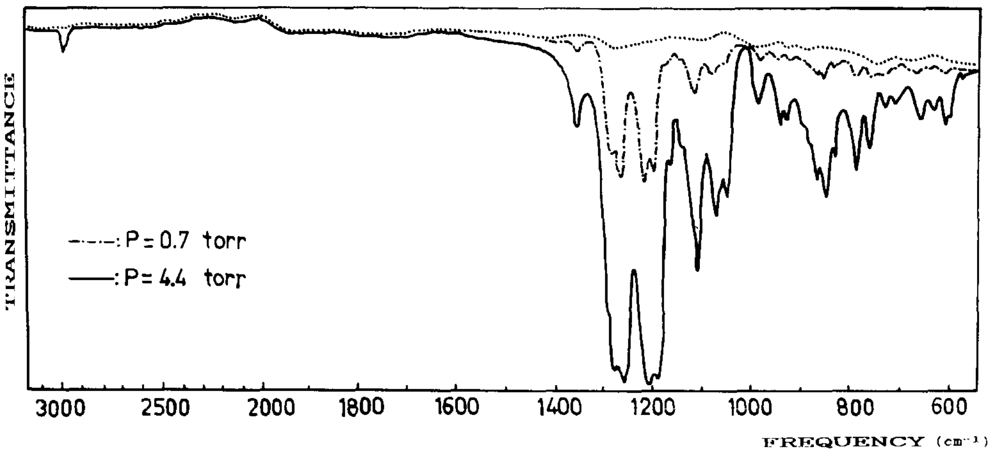

Fig. 1. Infrared spectrum of $CF_3O(CHClCCl_2)F$.

TABLE 2. Infrared spectrum of $CF_3O(CHClCCl_2)F$

Frequency (cm^{-1})[a]	Tentative assignment	Frequency (cm^{-1})[a]	Tentative assignment
2998 (vw)	C–H	943 (w)	C–C
		928 (w)	C–C
1358 (m)	C–C		
1289 (vs)	CF_3	868 (m)	C–Cl
1271 (vs)	CF_3	852 (m)	C–Cl
1221 (vs)	CF_3	831 (m)	C–Cl
1200 (vs)	CF_3	789 (m)	C–Cl
		761 (m)	C–Cl
1115 (s)	C–F	731 (w)	C–Cl
1074 (m)	C–F	712 (w)	C–Cl
		660 (w)	C–Cl
1053 (m)	C–O	631 (w)	C–Cl
986 (w)	C–O	610 (w)	C–Cl

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

complete consumption of $CHClCCl_2$, is illustrated in Fig. 1. The corresponding bands frequencies are listed in the Table 2. These frequencies indicate the presence of the structural groups CF_3, C–F, C–O, C–C and C–Cl, suggesting that the compound distilling at 243 K is $CF_3O(CHClCCl_2)F$. A comparison of its infrared spectrum with that of $CF_3O(CHClCHCl)F$ [1] supports this supposition.

Additional support to the characterization of $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)F$ was obtained by chromatographic determination of the relative molecular mass of the fraction distilling between 153 and 193 K and that distilling between 193 and 243 K, when all the $CHClCCl_2$ was consumed as confirmed by infrared spectra. The corresponding values were 152 ± 9 and 230 ± 14. The theoretical values of the relative molecular masses of $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)F$ are 150.35 and 235.35, respectively.

The residue remaining at 243 K was identified as $CF_3O(CHClCCl_2)_{n \geqslant 2}OCF_3$ by its infrared bands at 3000 (w), 1358 (m), 1286 (s), 1262 (vs), 1254 (vs sh), 1222 (vs), 1201 (s), 1150 (m), 1108 (s), 1044 (s), 985 (m), 868 (vs), 829 (vs), 759 (s) and 725 (m) cm^{-1}. The strong absorption bands at 1286–1201 cm^{-1}, a characteristic of the CF_3 group in compounds such as CF_3OF [15] and CF_3OOCF_3 [16], indicate the presence of the CF_3O grouping. The strong absorption bands at 884–759 cm^{-1}, a characteristic of compounds such as $CHClCCl_2$, indicate the presence of C–Cl and $C-Cl_2$ groups.

The infrared spectra of residues from different runs at 243 K were very similar, as expected for mixtures of compounds belonging to the same homologous series [17].

The assumption that $n \geqslant 2$ was derived from the following observations:

1. The formation of CF_3OOCF_3 was not observed, indicating that $CF_3O\cdot$ radicals were almost completely removed by reaction with trichloroethene, forming $CF_3O(CHClCCl_2)\cdot$ radicals.
2. The average number of alkene molecules consumed per CF_3OF increased with increasing ratio of the initial concentration of alkene to that of CF_3OF.
3. Small amounts of colourless liquid appeared when $[CHClCCl_2] \gg [CF_3OF]$, indicating telomerization of $CHClCCl_2$.

The introduction of O_2 into the reaction vessel at the beginning of the reaction changed its course, producing oxidation of $CHClCCl_2$ to $CHCl_2C(O)Cl$.

The data arising from nine experiments are summarized in Table 3, where Δt is the reaction time, Δp is the pressure decrease, E is $CHClCCl_2$ and the indices i and f signify initial and final. The quantity S_1 is the sum $\{[CHClCCl_2]_f + [CF_3O(CHClCCl_2)F]\}$ and S_2 is

TABLE 3. Analytical data for nine experiments at 303.8 K $\{E = [CHClCCl_2], A = [CHClFCCl_2F], B = [CF_3O(CHClCCl_2)F], S_1 = E_f + B, S_2 = \Sigma^n_{i \geqslant 2}[CF_3O(CHClCCl_2)_iOCF_3]\}$

Run No.	Δt (min)	Δp	$[CF_3OF]_i$	$[CF_3OF]_f$	E_i	E_f	A	(a_A)[a]	S_1	(a_B)[a]	S_2	(a_s)[a]
						Torr						
5	11.5	10.2	42.0	31.8	10.3	0	*		10.3	(100)	*	
9	14.0	5.4	31.2	25.9	5.3	0	*		5.2	(100)	*	
4	121.8	16.4	21.2	5.6	16.7	0	1.3	(8)	12.6	(82)	1.4	(9)
2	180.0	16.7	19.0	3.7	16.7	0	1.4	(9)	12.9	(83)	1.2	(8)
13	2.8	2.1	19.8	17.6	39.2	–[b]	*		39.0	(100)	*	
14	5.6	1.5	9.0	7.6	44.0	–[b]	*		44.2	(100)	*	
7	181.0	12.8	10.1	0	45.0	–[b]	2.1	(20)	38.3	(60)	2.0	(20)
6	179.0	11.8	8.9	0	44.6	–[b]	1.8	(20)	38.0	(58)	1.9	(21)
18	180.0	18.2	7.0	0	58.5	–[b]	1.8		43.7		–[c]	

*Concentration $\ll 1$ Torr undetectable by our analysis method.

[a] a_A, a_B, a_s = relative amounts (%) of A, B and S_2, taking $[B] = S_1 - (E_i - \Delta p)$, when $E_f \neq 0$.

[b] Concentration not determined.

[c] Residue non-volatile at 303.8 K.

the sum of recombination products $\Sigma_{i\geqslant 2}^{n}[\mathrm{CF_3O\text{-}(CHClCCl_2)}_i\mathrm{OCF_3}]$.

From these data it can be seen that:

$$[\mathrm{CHClCCl_2}]_{\mathrm{consumed}}=\Delta p$$

$$[\mathrm{CHClFCCl_2F}]=\sum_{i\geqslant 2}^{n}[\mathrm{CF_3O(CHClCCl_2)}_i\,\mathrm{OCF_3}]$$

$$[\mathrm{CF_3OF}]_{\mathrm{consumed}}$$

$$=2[\mathrm{CHClFCCl_2F}]+[\mathrm{CF_3O(CHClCCl_2)F}]$$

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