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Kinetics and Mechanism of the Thermal Gas-phase Reaction between Trifluoromethylhypofluorite, CF_3OF, and Trichloroethene

Zdzislaw Czarnowski and Joanna Czarnowski
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicades, Casilla de Correo 16, Sucursal 4, 1900 La Plata, Argentina

The thermal gas-phase addition of CF_3OF to $CHClCCl_2$ has been studied between 284 and 324.0 K. The initial pressure of CF_3OF was varied between 7 and 57.8 Torr [1 Torr = (101 325/760) Pa] and that of $CHClCCl_2$ between 3.4 and 45 Torr. $CF_3O(CHClCCl_2)F$ was the main product. Other products, formed in minor amounts, were $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)_{n\geqslant 2}OCF_3$.

The reaction was a homogeneous chain reaction not affected by the total pressure. In the presence of O_2 the oxidation of trichloroethene to $CHCl_2C(O)Cl$ occurred. Introduction of CCl_3F to the reaction system initiated the addition of this halomethane to trichloroethene.

The basic steps of the reaction were: generation of radicals $CF_3O^{\bullet}$ and $CHClFCCl_2^{\bullet}$ in the bimolecular process between CF_3OF and $CHClCCl_2$, (rate constant k_1), generation of telomeric radicals $CF_3O(CHClCCl_2)^{\bullet}$ by addition of $CF_3O^{\bullet}$ to trichloroethene, abstraction of fluorine atom from CF_3OF by $CHClFCCl_2^{\bullet}$ and $CF_3O(CHClCCl_2)^{\bullet}$, (rate constant k_4), polymeric chain propagation by further successive additions of telomeric radicals to another molecule of trichloroethene, (rate constant k_5), and recombination of telomeric radicals.

Trifluoromethylhypofluorite, CF_3OF, is a versatile electrophilic fluorinating agent used for preparative purposes.[1] The reactivity of CF_3OF with some simple alkenes has been studied by Johri and DesMarteau.[2] The reported main products of the additions of CF_3OF to CHClCHCl, CH_2CCl_2, CF_2CCl_2 and CF_3CFCF_2 were $CF_3O(CHClCHCl)F$, $CF_3O(CH_2CCl_2)F$, $CF_3O(CF_2CCl_2)F$ and $CF_3OCF_2CF_2CF_3$, respectively.

The kinetic studies of the gas-phase thermal addition of CF_3OF to the double bond of the hexafluoropropene,[3] perfluorobut-2-ene,[4] and 1,1-dichlorodifluoroethene,[5] showed that these three reactions have the following basic steps in common: the generation of radical $CF_3O^{\bullet}$ in the bimolecular process between CF_3OF and alkene, E, the formation of a telomeric radical $CF_3O(E)^{\bullet}$ by addition of $CF_3O^{\bullet}$ to the alkene and the abstraction of the fluorine atom from CF_3OF by the telomeric radical $CF_3O(E)^{\bullet}$ accompanied by a simultaneous generation of another radical $CF_3O^{\bullet}$.

In this work the study of the thermal gas-phase reaction between CF_3OF and trichloroethene has been undertaken in order to obtain the kinetic data on the elementary reactions involved.

Experimental

The reaction proceeded with a pressure decrease. The experiments were performed in a grease-free static system allowing pressure measurements at constant volume and temperature. Two spherical quartz bulbs of 180 cm^3, one filled with small pieces of quartz tubing, were used as reaction vessels. The corresponding surface area-to-volume ratios were 0.75 and 4.7 cm^{-1}. The pressure was measured with a quartz spiral gauge and the temperature was maintained to within ± 0.1 K using a Lauda thermostat.

The infrared (IR) spectra were recorded on a Perkin-Elmer 325 spectrometer using a 10 cm cell with sodium chloride windows.

All reactants were commercial products. CF_3OF was washed with 0.1 mol dm^{-3} NaOH solution and filtered at 80 K.[6] Trichloroethene was purified by several trap-to-trap distillations on a vacuum line, retaining each fraction distilling between 263 and 273 K. N_2 was bubbled through 98% analytical-grade H_2SO_4 and passed slowly through a Pyrex coil at liquid-air temperature. Analytical-grade CCl_3F was used without further purification.

Experiments were made at 284, 293.8, 303.8, 313.8 and 324 K. The initial pressure of CF_3OF was varied between 7 and 57.8 Torr and that of $CHClCCl_2$ between 3.4 and 45.0 Torr. Some experiments were made in presence of N_2, varying its pressure within 526–552 Torr, as well as in the presence of CCl_3F, varying its pressure within 393.6–421 Torr, and in the reaction vessel with a larger surface area-to-volume ratio.

Results

The reaction was a homogeneous chain reaction. The main product was $CF_3O(CHClCCl_2)F$. The other products, formed in minor amounts, were $CHClFCCl_2F$ and $CF_3O(CHClCCl_2)_{n\geqslant 2}OCF_3$.

For analysing the reaction mixture the reaction vessel was cooled to liquid-air temperature and the mixture separated by fractional distillation.

The non-consumed CF_3OF was separated at 153 K. The fraction volatile at 193 K consisted of $CHClFCCl_2F$, identified by comparing its IR spectrum with that of CCl_2FCCl_2F.[7] The fraction that was volatile at 243 K was composed of trichloroethene and $CF_3O(CHClCCl_2)F$. In the experiments carried out until the complete consumption of trichloroethene, this fraction consisted of pure $CF_3O(CHClCCl_2)F$, identified by comparing its infrared absorption band frequencies at 2998 w, 1358 m, 1289 vs sh, 1271 vs, 1221 vs, 1200 vs sh, 1115 s, 1074 m, 1053 m, 986 w, 928 w, 868 m, 852 s, 831 w, 789 s, 761 m, 731 w, 712 w, 660 w, 631 w and 610 w cm^{-1} with those of $CF_3O(CHClCHCl)F$.[2]

The residue at 243 K was identified as $CF_3O(CHClCCl_2)_{n\geqslant 2}OCF_3$ by its infrared bands frequencies 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}, characteristic of the CF_3 group in compounds such as CF_3OF[8] and $CF_3O_2CF_3$[9] indicate the presence of CF_3O grouping. The strong absorption bands at 884–759 cm^{-1}, characteristic of compounds such as $CHClCCl_2$, suggest the presence of C—Cl and $C—Cl_2$ groups.

The assumption that $n \geqslant 2$ was based on the following

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Table 1 Analytical data from 13 experiments $\{E = [CHClCCl_2], S_1 = E_f + [CF_3O(CHClCCl_2)F], S_2 = \sum_{i\geq 2}^{n} [CF_3O(CHClCCl_2)_iOCF_3)]\}$

run	T/K	Δp^a	$[CF_3OF]_i^a$	$[CF_3OF]_f^a$	E_i^a	E_f^a	$[CHClFCCl_2F]^a$	S_1^a	S_2^a
31	284.0	5.9	22.2	16.3	6.0	0	—[b]	5.8	—[b]
15	293.8	2.4	21.2	18.7	13.9	—[c]	—[b]	13.8	—[b]
19	293.8	4.4	32.7	28.4	4.6	0	—[b]	4.3	—[b]
22	293.8	8.0	5.3	0	42.3	—[c]	1.5	36.5	1.4
2	303.8	16.7	19.0	3.7	16.7	0	1.4	12.9	1.2
4	303.8	16.4	21.2	5.6	16.7	0	1.3	12.6	1.4
5	303.8	10.2	42.0	31.8	10.3	0	—[b]	10.3	—[b]
6	303.8	11.8	8.9	0	44.6	—[c]	1.8	38.0	1.9
7	303.8	12.8	10.1	0	45.0	—[c]	2.1	38.3	2.0
9	303.8	5.4	31.2	25.9	5.3	0	—[b]	5.2	—[b]
13	303.8	2.1	19.8	17.6	39.2	—[c]	—[b]	39.0	—[b]
39	313.8	3.9	12.6	8.8	3.9	0	—[b]	3.7	—[b]
43	313.8	16.2	14.9	0	34.2	—[c]	1.7	29.5	1.6

[a] in Torr; [b] concentration <1 Torr undetectable by our analysis method; [c] concentration not determined.

observations: (1) The formation of $CF_3O_2CF_3$ was not observed, indicating that the radicals $CF_3O^{\bullet}$ were very rapidly scavenged by $CHClCCl_2$. It suggests that the chain termination occurred by the recombination of telomeric radicals $CF_3O(CHClCCl_2)^{\bullet}$; (2) The average amount of alkene consumed per CF_3OF increased with the increasing ratio of the initial concentration of alkene to that of CF_3OF; (3) Small amounts of colourless liquid appeared at temperature $T \leqslant 293.8$ K and $[CHClCCl_2]_i/[CF_3OF]_i \geqslant 1.5$, where i = initial, indicating telomerization of $CHClCCl_2$.

The IR spectra of residues at 243 K, obtained from different runs, were very similar, as expected for the mixtures of compounds belonging to the same homologous series,[10] where it is sufficient to identify only one compound in order to determine the successive members of a series, which differ only by some increasing property, like alkene unit in this case.

The data of 13 experiments are summarized in the Table 1, where Δp is the pressure decrease, E is $[CHClCCl_2]$, indices i and f signify initial and final. S_1 is the sum $\{[CHClCCl_2] + [CF_3O(CHClCCl_2)F]\}$ and S_2 is the sum of the recombination products $\sum_{i\geq 2}^{n}[CF_3O(CHClCCl_2)_iOCF_3]$.

From these data it can be seen that:

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

$$[CHClFCCl_2F] = \sum_{i\geq 2}^{n}[CF_3O(CHClCCl_2)_iOCF_3]$$

$$[CF_3OF]_{consumed} = 2[CHClFCCl_2F] + [CF_3O(CHClCCl_2)F]$$

The global reaction can be represented by the equation:

$$(1 + a)CF_3OF + [1 + (1 + n)a]CHClCCl_2 = aCHClFCCl_2F + CF_3O(CHClCCl_2)F + a\sum_{i\geq 2}^{n}CF_3O(CHClCCl_2)_iOCF_3.$$

At the first stage of the reaction, where

$$[CF_3O(CHClCCl_2)F] \gg [CHClFCCl_2F] + \sum_{i\geq 2}^{n}[CF_3O(CHClCCl_2)_iOCF_3]$$

it may be assumed that $\Delta p \approx [CF_3OF]_{consumed}$. The error thus introduced in the value of the concentration of CF_3OF falls within the measurement error limits.

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

The addition of CCl_3F, supposed to act as an inert gas, increased the consumption of alkene and new bands appeared in the IR spectra of the reaction mixture. Within this work no attempt was made to identify the corresponding products.

Discussion

To explain the experimental results the following mechanism was postulated:

$$CF_3OF + CHClCCl_2 = CHClFCCl_2^{\bullet} + CF_3O^{\bullet} \quad (1)$$

$$CHClFCCl_2^{\bullet} + CF_3OF = CHClFCCl_2F + CF_3O^{\bullet} \quad (2)$$

$$CF_3O^{\bullet} + CHClCCl_2 = CF_3O(CHClCCl_2)^{\bullet} \quad (3)$$

$$CF_3O(CHClCCl_2)^{\bullet} + CF_3OF = CF_3O(CHClCCl_2)F + CF_3O^{\bullet} \quad (4)$$

$$CF_3O(CHClCCl_2)_i^{\bullet} + CHClCCl_2 = CF_3O(CHClCCl_2)_{i+1}^{\bullet} \quad (i \geqslant 1) \quad (5)$$

$$CF_3O(CHClCCl_2)_i^{\bullet} + CF_3O(CHClCCl_2)_j^{\bullet} = CF_3O(CHClCCl_2)_{i+j}OCF_3 \quad (6)$$

$$(i = j = 1, 2, 3 \ldots \quad \text{and} \quad i + j = n \geqslant 2)$$

Other possible steps were considered but did not appear necessary to explain the results.

All steps of the chain growth were assumed to have the same rate constant, k_5, similar to the rate constant for the polymerization of trichloroethene. The recombination rate constant, k_6, was assumed to be equal for all radicals.

The rate constants k_2 and k_4 were considered to be similar and independent of radical structure. This supposition is supported by the room-temperature values of the rate constants

Table 2 Derived rate constants

T/K	$C_1 \times 10^{4\,a}$	$C_2 \times 10^{3\,a}$	C_3	$C_4 \times 10^{5\,a}$	$k_6 \times 10^{-7\,a}$	$k_1 \times 10^{5\,a}$	$k_4 \times 10^{-2\,a}$	$k_5{}^a$
284.0	0.69	0.62	0.78	2.9	3.38	2.3	4.8	35.4
293.8	1.23	1.16	0.76	4.8	3.27	4.1	6.44	45.5
303.8	2.28	2.3	0.80	8.1	3.17	7.6	8.6	56.9
313.8	3.96	4.4	0.82	13.0	3.07	13.2	11.7	70.2
324.0	7.12	8.1	0.94	22.5	2.97	23.7	14.4	84.3

[a] In $Torr^{-1}$ min^{-1}.

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Table 3 Experimental and calculated rates of the consumption of $CHClCCl_2$

run	T/K	$[CF_3OF]_i$/Torr	$[CHClCCl_2]_i$/Torr	Δt/min	Δp/Torr	V_{exp}/Torr min^{-1}	V_{cal}/Torr min^{-1}
27	284.0	30.1	12.8	4.5	1.2	0.267	0.276
				11.3	2.9	0.250	0.246
				18.7	4.5	0.216	0.206
				36.2	7.3	0.160	0.162
28	284.0	32.3	8.7	8.1	2.1	0.259	0.255
				15.15	3.7	0.227	0.208
				27.4	5.7	0.163	0.164
				44.1	7.6	0.114	0.113
29	284.0	41.2	9.4	4.5	1.7	0.378	0.403
				9.0	3.3	0.356	0.348
				14.95	5.2	0.319	0.289
				22.0	6.8	0.227	0.228
30	284.0	57.6	11.9	2.6	2.0	0.769	0.765
				5.1	3.7	0.680	0.677
				8.3	5.8	0.656	0.585
				12.5	7.8	0.476	0.482
				15.4	9.0	0.414	0.395
				20.7	10.6	0.302	0.308
31	284.0	22.2	6.0	13.1	1.4	0.107	0.121
				28.1	2.9	0.100	0.096
				42.7	4.0	0.075	0.074
				57.9	4.8	0.053	0.057
16	293.8	21.2	13.9	8.7	2.4	0.276	0.278
				21.4	5.0	0.205	0.207
17	293.8	44.6	8.4	4.2	3.2	0.762	0.778
				9.5	6.2	0.566	0.548
				15.0	8.0	0.327	0.327
18	293.8	38.8	11.0	3.55	2.4	0.676	0.713
				6.8	4.4	0.615	0.592
				10.8	6.3	0.475	0.483
				14.8	7.9	0.400	0.385
19	293.8	32.7	4.6	4.3	1.6	0.372	0.385
				8.8	3.0	0.311	0.295
				13.9	4.0	0.204	0.205
20	293.8	36.9	22.3	2.05	1.8	0.878	0.880
				5.0	4.0	0.745	0.773
				7.2	5.5	0.682	0.680
				9.9	7.2	0.630	0.604
21	293.8	30.0	10.6	4.2	1.9	0.452	0.464
				8.3	3.5	0.390	0.390
				14.2	5.5	0.339	0.318
				21.2	7.3	0.257	0.245
1[a]	303.8	21.0	14.8	2.0	1.2	0.600	0.574
				8.95	4.0	0.403	0.459
				20.5	7.5	0.303	0.302
2[a]	303.8	19.0	16.7	7.5	3.4	0.453	0.449
				25.8	8.0	0.251	0.259
3[b]	303.8	20.2	16.8	7.8	3.7	0.474	0.493
				26.3	8.6	0.265	0.281
4	303.8	21.2	16.7	9.7	4.7	0.485	0.507
				17.4	7.3	0.338	0.323
5	303.8	42.0	10.3	1.7	2.5	1.471	1.513
				3.55	4.8	1.243	1.225
				5.25	6.6	1.059	0.976
6	303.8	8.9	44.6	5.6	1.5	0.268	0.262
				13.2	3.0	0.197	0.199
7	303.8	10.1	45.0	5.3	1.6	0.302	0.312
				30.4	6.2	0.183	0.179
8	303.8	28.2	13.3	2.5	2.1	0.840	0.868
				5.2	4.0	0.704	0.718
9	303.8	31.2	5.3	2.8	2.0	0.714	0.705
				5.3	3.4	0.560	0.531
				8.1	4.4	0.357	0.387
10	303.8	19.2	7.9	5.7	2.1	0.368	0.363
				14.1	4.2	0.250	0.260
11	303.8	9.2	7.9	14.2	1.3	0.092	0.109
				29.0	2.5	0.081	0.078
12	303.8	19.8	39.2	2.8	2.1	0.750	0.764
				5.5	3.9	0.667	0.630
37	313.8	23.9	11.3	2.1	2.4	1.143	1.128
				6.6	6.0	0.800	0.788
38	313.8	15.9	9.5	3.55	1.9	0.535	0.535
				8.15	3.8	0.413	0.391
39	313.8	12.6	3.9	6.0	1.5	0.250	0.256
				12.8	2.7	0.176	0.171
				20.9	3.5	0.099	0.107

(continued)

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Table 3 (*continued*)

run	T/K	$[CF_3OF]_i$/Torr	$[CHClCCl_2]_i$/Torr	Δt/min	Δp/Torr	V_{exp}/Torr min^{-1}	V_{cal}/Torr min^{-1}
40	313.8	8.8	20.3	4.5	1.3	0.289	0.286
				13.4	3.1	0.202	0.201
41	313.8	19.8	8.2	3.1	2.2	0.710	0.723
				5.95	3.7	0.526	0.547
42	313.8	7.0	3.4	13.8	1.2	0.087	0.089
				29.5	2.1	0.057	0.057
43	313.8	14.9	34.2	3.4	2.6	0.765	0.800
				7.5	5.1	0.610	0.563
46	324.0	18.2	7.0	1.7	1.8	1.059	1.028
				3.9	3.4	0.727	0.769
47	324.0	15.4	4.8	2.1	1.4	0.667	0.680
				4.4	2.6	0.522	0.506
49	324.0	21.4	6.0	0.85	1.2	1.412	1.325
				1.9	2.2	0.952	1.113
52	324.0	10.2	10.8	4.9	2.0	0.408	0.444
				11.5	3.8	0.273	0.281
53	324.0	8.2	20.4	1.95	1.0	0.513	0.467
				5.7	2.2	0.320	0.362

[a] These experiments were performed in the reactor with $S/V = 4.7$ cm^{-1}. [b] 526.2 Torr of N_2 was present.

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for the abstraction of fluorine atom from CF_3OF by $CF_3^{\bullet}$,[11] $C_2H_5^{\bullet}$[12] and $CF_3O(CF_2CCl_2)^{\bullet}$,[5] which are *ca.* 10^5 dm^3 mol^{-1} s^{-1}. The room-temperature rate constants for the abstraction of a chlorine atom from SF_5Cl by $SF_5CH_2CF_2^{\bullet}$, $SF_5CF_2CF_2^{\bullet}$ and $CF_2ClCF_2^{\bullet}$ have values of *ca.* 7×10^3 dm^3 mol^{-1} s^{-1}.[13]

The lack of formation of $CF_3O_2CF_3$ shows that the addition of $CF_3O^{\bullet}$ to the double bond is considerably faster than any other reaction of $CF_3O^{\bullet}$.[5,14–17] This behaviour of the CF_3O group is transmitted through the telomeric radicals $CF_3O(CHClCCl_2)_i^{\bullet}$, enhancing their additivity to the alkene.

The absence of a CF_3O group in the radical $CHClFCCl_2^{\bullet}$ appears to decrease its reactivity with respect to $CHClCCl_2$, favouring its scavenging by CF_3OF. The rate constants for the addition of radicals to alkenes vary with its electrophilic character. The addition of $CF_3^{\bullet}$ radicals to the alkene is *ca.* three orders of magnitude faster than that of $CH_3^{\bullet}$.[18]

The rate constant of the fluorine abstraction decreases when a second monomer unit is incorporated into the telomeric radical, removing progressively the CF_3O group from the radical center. This is, probably, due to the lowering of the electron-withdrawing effect of the CF_3 group, while the radical length is increasing. The potent electron withdrawing groups facilitate the halogen abstraction.[19]

Application of the steady-state approximation to the mechanism leads to the following rate equation:

$$-\mathrm{d}[CHClCCl_2]/\mathrm{d}t = 3k_1[CF_3OF][CHClCCl_2] + 2k_1 k_4/k_5[CF_3OF]^2 \times \{1 + (k_1 k_6)^{0.5}/k_5([CF_3OF]/[CHClCCl_2])^{0.5}\}^{-1} + k_5(k_1/k_6)^{0.5}[CF_3OF]^{0.5}[CHClCCl_2]^{1.5} \quad \text{(I)}$$

Data Treatment

The rate constants k_1 and k_4 were estimated taking k_6 equal to the collisional frequency factor $(60/RT) \times 10^{10}$ Torr^{-1} min^{-1} and using a program to calculate a and b from the equation $y = a + bx$, where $y = V_{exp}/([CF_3OF][CHClCCl_2])$, $a = 3k_1$, $b = k_4(k_1/k_6)^{0.5}$, and $x = ([CF_3OF]/[CHClCCl_2])^{0.5}$.

The above simplification of eqn. (I), is applicable only for $[CF_3OF] > [CHClCCl_2]$. The rate constant k_5 was derived introducing the estimated values for k_1, k_4 and k_6 into eqn. (I).

$C_1 = 3k_1$, $C_2 = 2k_1k_4/k_5$, $C_3 = (k_1k_6)^{0.5}/k_5$ and $C_4 = k_5(k_1/k_6)^{0.5}$, the composite constants from eqn. (I), were calculated with the estimated values of k_1, k_4, k_5 and k_6 and subsequently adjusted by iteration using a program for calculation of non-linear parameters. A set of parameters was selected that best compared the experimental reaction rate $\mathrm{d}p/\mathrm{d}t$ with eqn. (I). From these parameters the rate constants k_1, k_4 and k_5 were computed.

Table 2 presents the values of the constants obtained at different temperatures.

The following expressions for the rate constants k_1, k_4 and k_5 were obtained:

$$k_1 = (3.3 \pm 2) \times 10^6 \exp(-47.3 \pm 10 \text{ kJ mol}^{-1}/RT) \times \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_4 = (3.0 \pm 2) \times 10^9 \exp(-23.5 \pm 10 \text{ kJ mol}^{-1}/RT) \times \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_5 = (3.3 \pm 3) \times 10^7 \exp(-19.0 \pm 10 \text{ kJ mol}^{-1}/RT) \times \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The respective pre-exponential factors for addition of CF_3OF to C_4F_8[4] and to CF_2CCl_2[5] are 5.34×10^6 and 5×10^6. The corresponding activation energies are 58.2 and 40.6 kJ mol^{-1}.

The values of the room temperature rate constants for abstraction of fluorine atom from CF_3OF by radicals $CF_3^{\bullet}$,[11] $C_2H_5^{\bullet}$[12] and $CF_3OCF_2CCl_2^{\bullet}$[5] are 1.8×10^5, $\geqslant 6 \times 10^4$ and 1.4×10^5 dm^3 mol^{-1} s^{-1}, respectively.

In Table 3 are presented V_{exp} and V_{cal}, the experimental and calculated rates of the consumption of $CHClCCl_2$. Δt is the reaction time, Δp is the pressure decrease equal to the consumption of $CHClCCl_2$ and the index i signifies initial. V_{cal} was calculated using eqn. (I). The amount of CF_3OF consumed was taken equal to Δp in experiments where $[CF_3OF]_i > [CHClCCl_2]_i$ and, for the first stage of the reaction, where $[CF_3OF]_i < [CHClCCl_2]_i$. In both cases the amount of minor products formed was negligible with respect to that of $CF_3O(CHClCCl_2)F$ produced. The ratio of the consumption of alkene to that of CF_3OF is approximately unity. The error thus introduced in the concentration of CF_3OF falls within the experimental error limits.

Addition of CCl_3F and O_2

The observed increase of the consumption of alkene and the appeareance of new and unidentified bands in the IR spectra,

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when CCl_3F was added to the reaction system, could possibly be explained by the free radical initiated addition of CCl_3F to the double bond:

$$R^{\cdot} + CCl_3F = RCl + CCl_2F^{\cdot} \qquad (1)$$

$$CCl_2F^{\cdot} + CHClCCl_2 = \text{products} \qquad (2)$$

Other authors have reported that CCl_4 reacts with fluoroalkenes in presence of free radicals.[20,21]

The formation of $CHCl_2C(O)Cl$ in the presence of molecular O_2 indicated the free radical initiated oxidation of $CHClCCl_2$. The reported main product of the oxidation of CF_2CCl_2 in the presence of CF_3OF is $CF_2ClC(O)Cl$.[17]

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