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Kinetics and Mechanism of the Thermal Gas-Phase Oxidation of Tetrachloroethene by Molecular Oxygen in Presence of Trifluoromethylhypofluorite, CF_3OF

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The oxidation of tetrachloroethene by molecular oxygen in presence of CF_3OF has been studied at 314.0, 324.2, 334.1 and 344.3 K. The initial pressure of CF_3OF was varied between 2.0 and 8.2 Torr, that of CCl_2CCl_2 between 8.7 and 21.7 Torr, that of O_2 between 33.2 and 730.7 Torr. Several runs were made adding N_2 at pressure varying between 250.4 and 525.9 Torr. The major products were $CCl_3C(O)Cl$ and $COCl_2$. $CF_3OCCl_2C(O)Cl$, $CCl_2FC(O)Cl$, $CF_3OCCl_2CCl_2F$ and CCl_2FCCl_2F were formed in traces. The oxidation is a chain reaction. Its rate increases with total pressure. The following mechanism, where $E = CCl_2CCl_2$, $R = CCl_2FCCl_2$, $CF_3OCCl_2CCl_2$ or CCl_3CCl_2, $R' = CCl_2F$, CF_3OCCl_2 or CCl_3 and M = effective pressure, explains the experimental results:

1) $CF_3OF + E \rightarrow R + CF_3O$
2) $CF_3O + E \rightarrow R$
3, 7) $R + O_2 + M \rightarrow RO_2 + M$
4, 8) $2RO_2 \rightarrow 2RO + O_2$
5) $RO \rightarrow R'C(O)Cl + Cl$
6) $Cl + E \rightarrow CCl_3CCl_2$
9) $CCl_3CCl_2O \rightarrow CCl_3C(O)Cl + Cl$
10) $CCl_3CCl_2O \rightarrow CCl_3 + COCl_2$
11) $CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$
12) $CCl_3O_2 + RO_2 \rightarrow CCl_3O + RO + O_2$
13) $CCl_3O \rightarrow COCl_2 + Cl$
14) $2R \rightarrow$ recombination products,
15) $R + CF_3OF \rightarrow RF + CF_3O$

$k_9 = (3.0 \pm 1.4) \times 10^{13} \exp(-9.66 \pm 1 \text{ kcal mol}^{-1}/RT)\ \text{s}^{-1}$.

Introduction

In the previously studied reactions of CF_3OF with CF_2CCl_2 [1] and $CHClCCl_2$ [2] in presence of O_2, a low temperature oxidation of each alkene occurred, giving $CF_2ClC(O)Cl$ and $CHCl_2C(O)Cl$ as the major products. These works provided evidence that chlorine atoms can be generated in absence of light by the addition of CF_3OF to the double bond of chloroalkene.

To rationalize the experimental results of the oxidation of CF_2CCl_2 and $CHClCCl_2$ in presence of CF_3OF, the formation of free radicals $CF_3O^{\bullet}$ was postulated. The recent studies of the reactions of CF_3OF with haloalkenes (E) [3, 4] confirmed, that these reactions occur via a radical mechanism, in which radicals $CF_3O^{\bullet}$ and $F(E)^{\bullet}$ are formed by the homolytic cleavage of the O−F bond in the bimolecular reaction between CF_3OF and haloalkene. The radical $CF_3O^{\bullet}$ adds rapidly to the double bond, giving radical $CF_3O(E)^{\bullet}$. The formation of these radicals was detected by EPR and ENDOR. It was reported by other authors that the addition of $CF_3O^{\bullet}$ to the unsaturated system is the major reaction channel in these system [5−8].

Radicals $CF_3O^{\bullet}$ are formed in atmospheric oxidation of HCFCs and HFCs containing CF_3 group [9−19]. Tetrachloroethene is produced industrially in large amounts about 400 ktons yr^{-1} [20], and is used in metal degreasing, dry cleaning and as industrial solvent. It escapes into the atmosphere at 90−100% of the amount produced.

In this work a kinetic study of the oxidation of CCl_2CCl_2, initiated by the addition of CF_3OF to its double bond has been undertaken.

Experimental

The reaction proceeded with pressure decrease. The experiments were performed in a grease-free static system allowing pressure measurements at constant volume and temperature. A spherical quartz bulb of 270 cm^3 was used as a reaction vessel. The pressure was measured with a quartz spiral gauge and the temperature maintained within ±0.1 K using a Lauda thermostat. Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer using a 10 cm cell with sodium chloride windows.

The chromatograms were recorded on a Gow-Mac 625 gas chromatograph, provided with a gas-density balance detector, using a column of 5% SE-30 on chromosorb W-AW at 273 K. The carrier gas was N_2. The gas density balance responds directly in wt% if each peak area is multiplied by $F_j = M_j/(M_j - M_c)$, where M_j and M_c are the respective molecular weights of each component and the carrier gas, and then each corrected area is divided by the sum of all corrected areas [21].

All reactants were commercial products. CF_3OF was washed with 0.1 mol dm^{-3} NaOH solution and filtered at 80 K [22]. Tetrachloroethene was purified by several trap-to-trap distillations on a vacuum line, retaining each fraction distilling between 263 and 273 K. O_2 and N_2 were bubbled through 98% analytical-grade H_2SO_4 and passed slowly through a Pyrex coil at 123 K and at liquid-air temperature, respectively.

The reaction was followed by measuring the pressure decrease as a function of time. Experiments were made at 314.0, 324.2, 334.1 and 344.3 K. The initial pressure of CF_3OF was varied between 2.0 and 8.2 Torr, that of CCl_2CCl_2 between 8.7 and 21.7 Torr and that of O_2 between 33.2 and 730.7 Torr. Several runs were made in presence of N_2, varying its pressure from 250.4 to 525.9 Torr.

Results

The reaction was a chain reaction, approaching the order 1.5 with respect to both reactants. It indicated that both CF_3OF and CCl_2CCl_2 accounted for formation of the chain carriers. The reaction rate depended on the total pressure. The effects of O_2 and N_2 were similar. At the pressure of O_2 used in this work, the reaction attained the pseudo-zeroth-order condition with respect to O_2 as reactant, O_2 acting as a third body.

Within the temperature range used, and in absence of CF_3OF, no reaction between alkene and O_2 was observed after several hours.

In presence of CF_3OF the following products were identified: $CCl_3C(O)Cl$, $COCl_2$, $CF_3OCCl_2C(O)Cl$, $CCl_2FC(O)Cl$, $CF_3OCCl_2CCl_2F$ and CCl_2FCCl_2F. $CCl_3C(O)Cl$ and $COCl_2$ were the major products. The other products were formed in traces. The very strong infrared absorption band of CF_3OOCF_3 at 1166 cm^{-1} [23, 24] was never observed.

All the experiments were carried out until the total consumption of CCl_2CCl_2. For analyzing the reaction mixture of each experiment, the reaction vessel was rapidly cooled to liquid air temperature and the mixture separated by fractional condensation. N_2, if present, and non-consumed O_2 were separated as volatile at liquid air temperature. The fraction volatile at 153 K consisted of CF_3OF. $COCl_2$ was separated as volatile at 183 K. The fraction remaining as residue at 183 K was always separated in two samples I and II.

Chromatograms of each sample I were performed to determine the relative concentration of $CCl_3C(O)Cl$. In these chromatograms six peaks appeared. Their areas were $A_2(II) \ggg A_5(V) > A_1(I) > A_4(IV) > A_6(VI) > A_3(III)$, where the subscript signifies the ordinal number of each peak and the Roman numeral in the parenthesis designates the corresponding compound, characterized by its retention time. In the IR spectra of the samples I, only $CCl_3C(O)Cl$ was identified.

The samples II of all experiments were condensed together. To concentrate the more volatile products, the condensate was separated by fractional condensation at 195 and 223 K in three fractions Fr_1, Fr_2 and Fr_3.

Table 1. Analytical data of 25 experiments. The pressure differences Δp and the partial pressures are given in Torr. (%) are the respective yields of $CCl_3C(O)Cl$ and $COCl_2$ based on the initial pressure of CCl_2CCl_{2i}.

Run	T/K	Δp	CF_3OF_i	CF_3OF_f	CCl_2CCl_{2i}	O_{2i}	O_{2f}	$CCl_3C(O)Cl$[a]	(%)	$COCl_2$	(%)
17	314.0	4.0	7.0	6.9	9.5	56.3	50.8	8.1	(85.3)	3.0	(31.6)
12	314.0	5.0	6.5	6.4	12.0	100.1	93.2	10.1	(84.2)	3.6	(30.0)
16	314.0	5.5	6.3	6.3	12.8	199.0	191.7	11.0	(85.9)	3.8	(29.7)
15	314.0	4.7	7.0	6.9	10.9	287.7	281.6	9.2	(84.4)	3.0	(27.5)
14	314.0	5.2	8.2	8.1	12.0	400.6	393.8	10.2	(85.0)	3.8	(31.7)
24[b]	324.2	5.0	4.0	4.0	12.0	46.9	40.3	10.2	(85.0)	3.4	(28.3)
23	324.2	4.9	3.7	3.7	11.4	67.5	61.0	9.8	(86.0)	3.2	(28.1)
19	324.2	4.4	4.7	4.7	10.5	98.2	92.2	9.0	(85.7)	3.0	(28.6)
21	324.2	5.8	6.4	6.3	13.6	111.2	103.5	11.8	(86.8)	3.8	(27.9)
22	324.2	4.4	4.8	4.8	10.5	208.9	203.0	9.0	(85.7)	2.8	(26.7)
18	324.2	7.0	5.4	5.4	16.0	339.6	330.5	13.9	(86.9)	4.4	(27.5)
28	334.1	4.7	7.0	6.9	10.9	47.7	41.6	9.4	(86.2)	2.6	(23.9)
25	334.1	5.8	6.4	6.3	12.7	131.3	124.1	11.2	(88.2)	3.1	(24.4)
27	334.1	6.0	3.2	3.2	13.9	196.1	188.2	11.9	(85.6)	3.8	(27.3)
32	334.1	6.0	2.6	2.6	13.7	364.7	357.0	12.2	(89.1)	3.4	(24.8)
31	334.1	5.7	3.4	3.4	13.0	497.5	490.2	11.2	(86.2)	3.2	(24.6)
30	334.1	4.5	3.8	3.8	10.3	588.0	582.2	9.0	(87.4)	2.8	(27.2)
29	334.1	5.0	3.3	3.3	11.0	730.7	724.4	9.7	(88.2)	2.8	(25.5)
39	344.3	8.6	2.9	2.9	19.5	64.9	54.0	17.4	(89.2)	4.6	(23.6)
33	344.3	6.4	2.8	2.8	14.6	111.0	102.7	13.0	(89.0)	3.6	(24.7)
38	344.3	7.5	2.0	2.0	17.0	194.9	185.4	14.8	(87.1)	4.0	(23.5)
37	344.3	7.3	3.3	3.3	16.4	320.1	311.1	14.6	(89.0)	3.8	(23.2)
36	344.3	9.6	2.5	2.5	21.7	392.1	380.0	19.0	(87.6)	5.0	(23.0)
35	344.3	6.4	2.5	2.5	14.5	494.6	486.4	12.9	(89.0)	3.4	(23.4)
34	344.3	6.4	2.2	2.2	14.5	585.2	577.1	12.6	(86.9)	3.4	(23.4)

[a] $CCl_3C(O)Cl$ contains traces of $CF_3OCCl_2C(O)Cl$, $CCl_2FC(O)Cl$, $CF_3OCCl_2CCl_2F$ and CCl_2FCl_2F.
[b] This experiment was made in presence of 525.9 Torr of N_2.

In the chromatograms of the fraction Fr_1 four peaks appeared. Their areas were A_2(II) > A_1(I) > A_4(VI) > A_3(III). The peak 2 corresponded to $CCl_3C(O)Cl$. The retention times of the peaks 3 and 4 were equal to those of the peaks arisen by CCl_2FCCl_2F and $CF_3OCCl_2CCl_2F$ in the chromatograms performed under similar conditions in the previous study of the products of the addition of CF_3OF to tetrachloroethene in absence of O_2 [25]. In the IR spectra of the fraction Fr_1, the absorption bands of $CCl_2FC(O)Cl$ [26] were identified after subtracting the spectra of $CCl_3C(O)Cl$.

In the chromatograms of the fraction Fr_2 three peaks appeared. Their areas were A_1(II) $\gg$ A_3(V) $\gg$ A_2(IV). The peak 1 corresponded to $CCl_3C(O)Cl$. In the IR spectra of the fraction Fr_2, the absorption bands at 1806, 1287−1180 and 913−744 cm^{-1} were observed after subtracting the spectra of $CCl_3C(O)Cl$. These frequencies are characteristic to groups $C(O)Cl$, CF_3O [24, 27] and CCl_2, respectively, and are consistent with the presence of a compound having the structure $CF_3OCCl_2C(O)Cl$. The observed vibrational frequency of carbonyl group of pure $CCl_3C(O)Cl$ is $1812\ cm^{-1}$.

The fraction Fr_3 consisted of practically pure $CCl_3C(O)Cl$, as confirmed by IR spectra and chromatograms performed.

The analytical data of 25 experiments are summarized in Table 1. From these data the following can be deduced:

The formation of $CCl_3C(O)Cl$ increased with temperature. At 314.0, 324.2, 334.1 and 344.3 K, the mean yields of $CCl_3C(O)Cl$ and $COCl_2$, based on the initial pressure of CCl_2CCl_2, were 85 and 30, 86 and 27.9, 87.3 and 25.4, and 88.3 and 23.5, respectively. The consumption of CF_3OF was $<2\%$.

$$[CCl_2CCl_2]_{\text{consumed}} = [CCl_3C(O)Cl] + 0.5\,[COCl_2]$$

$$\Delta p_f(\text{final pressure decrease}) = 0.5\,[CCl_3C(O)Cl]\,.$$

Discussion

In order to propose a reaction mechanism the following reactions were considered: oxidations of CF_2CCl_2 [1] and $CHClCCl_2$ [2] in presence of CF_3OF and addition of CF_3OF to CCl_2CCl_2 [28] and to some other haloalkenes [3, 4, 29] in absence of O_2. The following reactions were also taken into account: oxidation of radicals $CCl_3^{\cdot}$ [30–34], reactions between peroxy radicals [35], chlorine atom elimination from $CCl_3O^{\cdot}$ [36], oxidation of radicals $CF_3CCl_2^{\cdot}$ [11, 19, 37–39], oxidation of CCl_3CCl_2H initiated by fluorine and chlorine atoms [40] and oxidations of CCl_2CCl_2 initiated by $OH^{\cdot}$ and chlorine atoms [41–45].

The following mechanism, where R = $CCl_2FCCl_2^{\cdot}$, $CF_3OCCl_2CCl_2^{\cdot}$ or $CCl_3CCl_2^{\cdot}$, was postulated to explain the experimental results:

1. $CF_3OF + CCl_2CCl_2 \rightarrow CCl_2FCCl_2^{\cdot} + CF_3O^{\cdot}$

2. $CF_3O^{\cdot} + CCl_2CCl_2 \rightarrow CF_3OCCl_2CCl_2^{\cdot}$

3a. $CCl_2FCCl_2^{\cdot} + O_2 + M \rightarrow CCl_2FCCl_2O_2^{\cdot} + M$

3b. $CF_3OCCl_2CCl_2^{\cdot} + O_2 + M \rightarrow CF_3OCCl_2CCl_2O_2^{\cdot} + M$

4a. $CCl_2FCCl_2O_2^{\cdot} + RO_2^{\cdot} \rightarrow CCl_2FCCl_2O^{\cdot} + RO^{\cdot} + O_2$

4b. $CF_3OCCl_2CCl_2O_2^{\cdot} + RO_2^{\cdot} \rightarrow CF_3OCCl_2CCl_2O^{\cdot} + RO^{\cdot} + O_2$

5a. $CCl_2FCCl_2O^{\cdot} \rightarrow CCl_2FC(O)Cl + Cl$

5b. $CF_3OCCl_2CCl_2O^{\cdot} \rightarrow CF_3OCCl_2C(O)Cl + Cl$

6. $Cl + CCl_2CCl_2 \rightarrow CCl_3CCl_2^{\cdot}$

7. $CCl_3CCl_2^{\cdot} + O_2 + M \rightarrow CCl_3CCl_2O_2^{\cdot} + M$

8. $CCl_3CCl_2O_2^{\cdot} + RO_2^{\cdot} \rightarrow CCl_3CCl_2O^{\cdot} + RO^{\cdot} + O_2$
9. $CCl_3CCl_2O^{\cdot} \rightarrow CCl_3C(O)Cl + Cl$
10. $CCl_3CCl_2O^{\cdot} \rightarrow CCl_3^{\cdot} + COCl_2$
11. $CCl_3^{\cdot} + O_2 + M \rightarrow CCl_3O_2^{\cdot} + M$
12. $CCl_3O_2^{\cdot} + RO_2^{\cdot} \rightarrow CCl_3O^{\cdot} + RO^{\cdot} + O_2$
13. $CCl_3O^{\cdot} \rightarrow COCl_2 + Cl$
14. $2R^{\cdot} \rightarrow$ Recombination products
15. $R^{\cdot} + CF_3OF \rightarrow RF + CF_3O^{\cdot}$.

The primary path is by the thermal reaction of CF_3OF with the CCl_2CCl_2. The rapid low temperature additions of CF_3OF to some simple alkenes were reported by other authors in studies made for preparative purposes [46, 47]. The recent studies of reactions of CF_3OF with haloalkenes (E) [3, 4], have shown that these reactions occur via a radical mechanism. The formation of the intermediate radicals was detected by EPR and ENDOR. The radicals $CF_3O^{\cdot}$ and $F(E)^{\cdot}$ are generated by homolytic cleavage of the O−F bond in the bimolecular reaction between CF_3OF and haloalkene. The radical $CF_3O^{\cdot}$ adds rapidly to the double bond giving the radical $CF_3O(E)^{\cdot}$.

A very rapid elimination of chlorine atoms by alkenes was reported for CCl_2CCl_2 [43] and C_2H_4 [48]. The addition of C_2H_4 to reaction system containing radicals $CCl_3^{\cdot}$ and O_2, eliminated so rapidly the free chlorine atoms produced in the process, that the ClO spectrum, observed in absence of C_2H_4, was not observed [49]. The addition of chlorine atoms to the double bond is the predominant removal mechanism of Cl in presence of CCl_2CCl_2 [50].

The lack of formation of CF_3OOCF_3 corroborates the results of previous works [51, 52], which indicate that the addition of the $CF_3O^{\cdot}$ radicals to the double bond of halogenated alkenes is considerably faster that any other reaction of $CF_3O^{\cdot}$. It was reported that the values of rate constants for the addition of $CF_3O^{\cdot}$ to several alkenes are of order of 10^{10} $dm^3\ mol^{-1}\ s^{-1}$ [5−8].

CF_3OF is a successful gas-phase scavenger for free radicals in absence of O_2, giving the corresponding stable fluoro analogues and $CF_3O^{\cdot}$ [3, 4, 53, 54]. But at the oxygen pressure used in this work, the radicals are principally scavenged by O_2. It was reported by other authors, that the fraction of ethyl radicals that escapes oxidation was <0.1% at 2 Torr of O_2 [55] and that the reaction rate constants for methyl and halomethyl radicals with O_2 exceed those for fluorine atom abstraction from CF_3OF by three to four orders of magnitude [53]. Then, the rate of reaction (15) must be very low, being the reaction (1) the principal pathway for the consumption of CF_3OF. A very small fraction of radicals $R^{\bullet}$ scavenged by CF_3OF, generates radicals $CF_3O^{\bullet}$, which initiate chains with chlorine atoms as chain carriers [29].

It was reported by other authors [40], that 85% of radicals $CCl_3CCl_2O^{\bullet}$, formed in the oxidation of CCl_3CCl_2H initiated by Cl and F atoms, eliminate Cl atom to give $CCl_3C(O)Cl$. The remaining 15% decompose via C−C bond scission to give radicals $CCl_3^{\bullet}$ and $COCl_2$. In this work the mean yields of $CCl_3C(O)Cl$ and $COCl_2$, based on initial pressure of CCl_2CCl_2, were found to be 85 and 30%, 86 and 27.9%, 87.3 and 25.4% and 88.3 and 23.5%, at 314.0, 324.2, 334.1 and 344.3 K, respectively. It points out that the other products originated from the parent CCl_2CCl_2, are formed in very small amounts.

It was assumed that $k_{3a} \approx k_{3b} \approx k_7 \approx k_{11}$, $k_{4a} \approx k_{4b} \approx k_8 \approx k_{12}$ and $k_{5a} \approx k_{5b} \approx k_9 \approx k_{13}$ and that the recombination constant k_{14} is equal for all radicals. The rate constant k_{15} was considered to be independent of the radical structure. This supposition is supported by the room-temperature values of the rate constants for the abstraction of a fluorine atom from CF_3OF by $CF_3^{\bullet}$, $C_2H_5^{\bullet}$, $CF_3O(CHClCCl_2)^{\bullet}$ and $CF_3O(CCl_2CCl_2)^{\bullet}$ reported to be 2×10^5 [53], $>6 \times 10^4$ [54], 2.3×10^5 [56] and $1{,}4 \times 10^5$ $dm^3\ mol^{-1}\ s^{-1}$ [28], respectively.

Applying the steady-state approximation to the mechanism, substituting $k_6[Cl][CCl_2CCl_2]$ by $k_9[RO^{\bullet}]$ and $k_2[CF_3O^{\bullet}][CCl_2CCl_2]$ by $k_1[CF_3OF][CCl_2CCl_2]$, for $k_1[CF_3OF][CCl_2CCl_2] \gg k_{15}[R^{\bullet}][CF_3OF]$, the following expression was obtained for the consumption of alkene:

$$-d[CCl_2CCl_2]/dt = 2\,k_1[CF_3OF][CCl_2CCl_2] + k_9[RO^{\bullet}]\,. \qquad (I)$$

The reaction is of pseudo-zeroth-order with respect to O_2 at the pressures of O_2 used in this work and depends on the total pressure. The velocity of elimination of radicals $R^{\bullet}$ by O_2, equal to the velocity of the chain generation of radicals $R^{\bullet}$, is proportional to the rate of formation of radicals $CF_3O^{\bullet}$, the concentration of alkene and f as defined by Troe [57]:

$$f = (k_0/k_\infty)(k_0/k_\infty + 1/[M])^{-1}\,F_c^{(1+\{\log(k_0[M]/k_\infty)\}^2)^{-1}} \qquad (II)$$

where k_0 is the third-order low-pressure-limit constant, k_∞ is the pseudo-first-order high-pressure-limit constant and F_c is the broadening factor which describes the pressure dependence of the stabilization of the energized adduct RO_2 on the effective pressure M. The concentrations of radicals $RO_2^{\bullet}$ and $RO^{\bullet}$ depend on the collisional deactivation efficiencies of O_2 and other gases present.

Then:

$$k_9[RO^{\bullet}] = k_7[R^{\bullet}][O_2][M] = k_p\,k_{15}[R^{\bullet}][CF_3OF][CCl_2CCl_2]f \qquad (III)$$

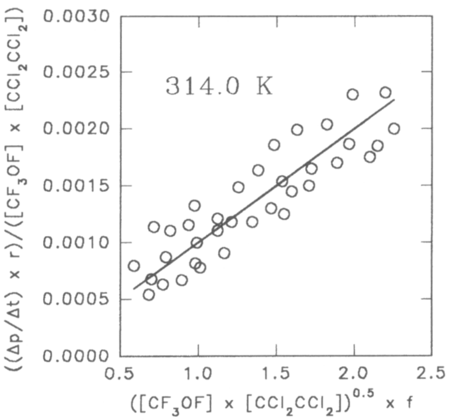

Fig. 1. The plot of $\{(\Delta p/\Delta t)r/[CF_3OF][CCl_2CCl_2]\}$ vs. $\{([CF_3OF][CCl_2CCl_2])^{0.5}f\}$ at 314.0 K, where Δp is the pressure decrease, Δt is the reaction time and $r = ([CCl_2CCl_2]_{initial}/\Delta p_{final})$. f is defined by Eq. (II). The value of the slope, equal to k, is given in the Table 2.

where:

$$k_p = k_9/k_6 \qquad \text{(IV)}$$

is the ratio of the rate constant for chlorine atoms generation to that for chlorine atoms elimination and

$$[R^\cdot] = (k_1/k_{14})^{0.5}[CF_3OF]^{0.5}[CCl_2CCl_2]^{0.5}\,. \qquad \text{(V)}$$

Substituting Eqs. (IV) and (V) into Eq. (III), one obtains:

$$k_9[RO^\cdot] = (k_9k_{15}/k_6)(k_1/k_{14})^{0.5}[CF_3OF]^{1.5}[CCl_2CCl_2]^{1.5}f\,. \qquad \text{(VI)}$$

Substituting Eq. (VI) into Eq. (I), the following rate of the consumption of alkene is obtained:

$$-d[CCl_2CCl_2]/dt = 2\,k_1[CF_3OF][CCl_2CCl_2] + (k_9k_{15}/k_6)(k_1/k_{14})^{0.5}[CF_3OF]^{1.5}[CCl_2CCl_2]^{1.5}f\,. \qquad \text{(VII)}$$

Data treatment

The composite constant from Eq. (VII):

$$k = (k_9k_{15}/k_6)(k_1/k_{14})^{0.5} \qquad \text{(VIII)}$$

was obtained as a slope, plotting $\{(\Delta p/\Delta t)r/[CF_3OF][CCl_2CCl_2]\}$ as a function of $\{[CF_3OF][CCl_2CCl_2]\}^{0.5}f$, where $r = ([CCl_2CCl_2]_{initial}/\Delta p_{final})$ and f is defined by Eq. (II). The plots at 314.0, 324.2, 334.1 and 344.3 K are illustrated at Figs. 1−4, respectively.

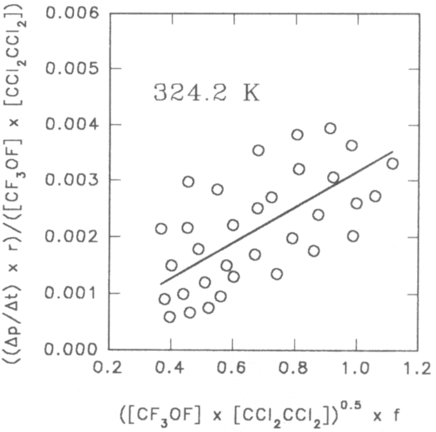

Fig. 2. The plot of $\{(\Delta p/\Delta t)r/[CF_3OF][CCl_2CCl_2]\}$ vs. $\{([CF_3OF][CCl_2CCl_2])^{0.5}f\}$ at 324.2 K, where Δp is the pressure decrease, Δt is the reaction time and $r = ([CCl_2CCl_2]_{\text{initial}}/\Delta p_{\text{final}})$. f is defined by Eq. (II). The value of the slope, equal to k, is given in the Table 2.

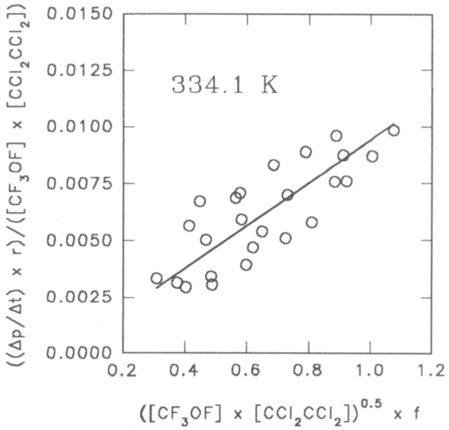

Fig. 3. The plot of $\{(\Delta p/\Delta t)r/[CF_3OF][CCl_2CCl_2]\}$ vs. $\{([CF_3OF][CCl_2CCl_2])^{0.5}f\}$ at 334.1 K, where Δp is the pressure decrease, Δt is the reaction time and $r = ([CCl_2CCl_2]_{\text{initial}}/\Delta p_{\text{final}})$. f is defined by Eq. (II). The value of the slope, equal to k, is given in the Table 2.

Lacking the data for the radical $CCl_3CCl_2^\bullet$, the values of k_0, k_∞ and F_c, derived from the temperature dependent expression for the termolecular process $CCl_3^\bullet + O_2 + M = CCl_3O_2^\bullet + M$ [33], were used to calculate f.

The following expression was used to calculate the effective pressure M:

$$M = [CCl_2CCl_2] + [CCl_3C(O)Cl] + 0.42[CF_3OF] + 0.4[COCl_2] + 0.25[O_2] + 0.21[N_2]\,.$$

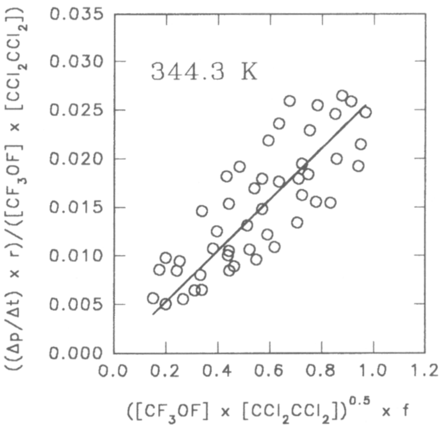

Fig. 4. The plot of $\{(\Delta p/\Delta t)r/[CF_3OF][CCl_2CCl_2]\}$ vs. $\{([CF_3OF][CCl_2CCl_2])^{0.5}f\}$ at 344.3 K, where Δp is the pressure decrease, Δt is the reaction time and $r = ([CCl_2CCl_2]_{\mathrm{initial}}/\Delta p_{\mathrm{final}})$. f is defined by Eq. (II). The value of the slope, equal to k, is given in the Table 2.

Table 2. Constants used to calculate the consumption rates od CCl_2CCl_2 at different temperatures.

T (K)	$k_1/10^{-5}$ (Torr^{-1} min^{-1})	$k_0/10^{4}$ (Torr^{-2} min^{-1})	$k_\infty/10^{6}$ (Torr^{-1} min^{-1})	$k/10^{-3}$ (min^{-1})
314.0	0.259	2.8	4.56	0.997
324.2	0.54	2.16	4.27	3.14
334.1	1.05	1.69	4.0	9.39
344.3	2.014	1.32	3.76	26.3

The relative collisional deactivation efficiency factors with respect to that of CCl_2CCl_2, taken as unity, were obtained for each gas from the corresponding collisional efficiencies, derived from the correlation between the boiling point of a third body and the association rate of two species [58]. It was reported that C_2H_4 is 3.16 and 4 times more effective than O_2 [59] and N_2 [60], respectively.

For F_c the value of 0.6 was taken. The values of k_0, k_∞, k and k_1, the rate constant for the addition of CF_3OF to CCl_2CCl_2 obtained previously [28], are given in the Table 2.

The results of the experiments are presented in the Table 3. In this table Δt is the reaction time, Δp is the pressure decrease, and subscripts i and f signify initial and final. The amounts of CF_3OF consumed at $\Delta t = t_n - t_{n-1}$ were computed, point by point, by $CF_3OF_n\{1-\exp(-k_1\Delta t[CCl_2CCl_2]_m)\}$, where $n = 1, 2, 3$ ... and $[CCl_2CCl_2]_m$ is the mean pressure of alkene in the

Table 3. The observed rate of reaction and the calculated rate of consumption of CCl_2CCl_2 divided by $r = [CCl_2CCl_2]_i/\Delta p_f$.

Run	T/K	CF_3OF_i/ Torr	CCl_2CCl_{2i}/ Torr	O_{2i}/ Torr	Δp_f/ Torr	Δt/ min	Δp/ Torr	V_{obs}/ Torr min^{-1}	V_{cal}/ Torr min^{-1}
17	314.0	7.0	9.5	56.3	4.0	31.50	0.7	0.022	0.020
						89.95	1.5	0.014	0.014
						181.70	2.3	0.009	0.009
12	314.0	6.5	12.0	100.1	5.0	31.40	1.1	0.035	0.033
						68.30	2.1	0.027	0.022
						119.40	2.7	0.012	0.014
16	314.0	6.3	12.8	199.0	5.5	30.10	1.4	0.047	0.047
						59.20	2.2	0.027	0.031
						121.70	3.5	0.021	0.019
14	314.0	8.2	12.0	400.6	5.2	29.90	2.3	0.077	0.073
						59.00	3.4	0.038	0.032
						118.70	4.2	0.012	0.015
24[a]	324.2	4.0	12.0	46.9	5.0	26.30	1.9	0.072	0.079
						59.35	3.2	0.039	0.037
						117.90	4.2	0.017	0.014
19	324.2	4.7	10.5	98.2	4.4	29.80	1.3	0.044	0.040
						59.80	2.1	0.027	0.024
						121.05	2.9	0.013	0.014
22	324.2	4.8	10.5	208.9	4.4	28.90	1.6	0.055	0.057
						59.60	2.5	0.029	0.030
						118.80	3.5	0.017	0.014
18	324.2	5.4	16.0	339.6	7.0	16.30	2.6	0.160	0.173
						30.20	3.8	0.086	0.094
						62.20	5.4	0.050	0.047
28	334.1	7.0	10.9	47.7	4.7	13.80	2.0	0.145	0.141
						29.30	3.0	0.065	0.063
						59.70	3.8	0.026	0.028
26	334.1	3.6	8.7	98.6	3.8	30.80	1.4	0.045	0.050
						68.40	2.3	0.024	0.025
						124.10	3.0	0.013	0.011
30	334.1	3.8	10.3	588.0	4.5	21.8	3.0	0.138	0.134
						49.10	3.9	0.033	0.028
						89.10	4.2	0.007	0.008
29	334.1	3.3	11.0	730.7	5.0	23.00	3.0	0.130	0.149
						60.40	4.5	0.040	0.032
						119.25	4.8	0.005	0.005
40	344.3	3.4	15.7	33.2	6.9	6.60	1.7	0.258	0.236
						14.55	2.8	0.138	0.156
						30.90	4.2	0.086	0.096
						60.80	5.6	0.047	0.042

[a] This experiment was performed in presence of 525.9 Torr of N_2.

Table 3. Continuation.

Run	T/K	CF_3OF_i/ Torr	CCl_2CCl_{2i}/ Torr	O_{2i}/ Torr	Δp_i/ Torr	Δt/ min	Δp/ Torr	V_{obs}/ Torr min^{-1}	V_{cal}/ Torr min^{-1}
38	344.3	2.0	17.0	194.9	7.5	5.70	1.5	0.263	0.258
						13.80	3.0	0.185	0.175
						23.80	4.3	0.130	0.109
36	344.3	2.5	21.7	392.1	9.6	4.2	3.0	0.714	0.683
						12.90	5.6	0.299	0.359
						20.50	6.9	0.171	0.179
35	344.3	2.5	14.5	494.6	6.4	5.95	2.2	0.370	0.393
						14.80	4.0	0.203	0.192
						22.10	4.8	0.110	0.090
						31.90	5.3	0.051	0.050
						45.40	5.7	0.030	0.027

interval Δt. It was assumed that other pathways of removing CF_3OF in presence of O_2 do not change significantly its concentration. As all the experiments were carried out to the total consumption of alkene, the amounts of CCl_2CCl_2 consumed were computed, point by point, multiplying Δp by $r = ([CCl_2CCl_2]_{\text{initial}}/\Delta p_{\text{final}})$. V_{obs} is equal to $\Delta p/\Delta t$, and V_{cal} is the rate of consumption of CCl_2CCl_2 calculated using Eq. (VII), divided by r.

In order to derive k_9 from Eq. (VIII), k_{14} was assumed to be equal to the collisional frequency factor (10^{10} dm^3 mol^{-1} s^{-1}) [61]. The room-temperature value of the rate constant for the addition of a chlorine atom to CCl_2CCl_2, reported by other authors [43], was used for k_6. The rate constants k_1 and k_{15} were calculated from the expressions obtained previously [28]:

$$k_1 = 3.16\pm0.6\times10^7 \exp(-15.2\pm1.7 \text{ kcal mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{15} = 3.7\pm0.5\times10^9 \exp(-6.0\pm1.1 \text{ kcal mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The values of $(5.74\pm1.4)\times10^6$, $(9.1\pm2.6)\times10^6$, $(1.46\pm0.4)\times10^7$ and $(2.22\pm0.4)\times10^7$ s^{-1} were obtained for k_9 at 314.0, 324.2, 334.1 and 344.3 K, respectively. The temperature dependence of the experimental rate constant k_9 can be expressed in the Arrhenius form (Fig. 5), as follows:

$$k_9 = (3.0\pm1.4)\times10^{13} \exp(-9.66\pm1 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}.$$

In a theoretical study of the decomposition of halogenated alkoxy radicals, the following kinetic parameters were calculated for the temperature range 240−260 K [62]:

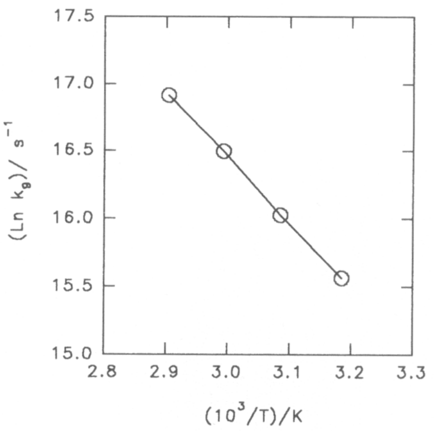

Fig. 5. Arrhenius plot of k_9.

$CCl_3O^\bullet$: $A=(4.09-4.49)\times10^{13}\ s^{-1}$; $E=9.7$ kcal mol^{-1}

$CFCl_2O^\bullet$: $A=(2.85–3.1)\times10^{13}\ s^{-1}$; $E=10.6$ kcal mol^{-1}

$CF_2ClO^\bullet$: $A=(2.85-3.13)\times10^{13}\ s^{-1}$; $E=12.4$ kcal mol^{-1}.

The lower limits determined for decomposition rates of $CCl_3O^\bullet$ and $CFCl_2O^\bullet$ are $1\times10^5\ s^{-1}$ at 233 K and $3\times10^4\ s^{-1}$ at 253 K, respectively, and correspond to the upper activation limits of 9.6 and 11 kcal mol^{-1} [36]. The reported values of the activation energies for the extrusion of chlorine atoms from $CFCl_2O^\bullet$ [63] at 238 and 298 K are 9.2 and 11.6 kcal mol^{-1}, respectively, and those for $CF_2ClCCl_2O^\bullet$ [1] and $CHCl_2CCl_2O^\bullet$ [2] are 9.4 and 9.45 kcal mol^{-1}, respectively.

This work provides evidence that free chlorine atoms can be released and $COCl_2$ formed as a consequence of the thermal addition of radical $CF_3O^\bullet$ to the double bond of tetrachloroethene in presence of O_2. The rate constant for chlorine atom detachment from the perchloroethyl oxy radical has been determined for the first time.

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