Thermal Gas Phase Hydrodehalogenation of Bromochlorodifluoromethane

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The thermal hydrodehalogenation of bromochlorodifluoromethane (Halon-1211; $CBrClF_2$) in the gas phase has been studied using a plug flow alumina reactor at atmospheric pressure over the temperature range 400–900 °C with residence times of 2–3 s and $CBrClF_2$/hydrogen molar intake ratios of *ca.* 10. Conversion of $CBrClF_2$ starts at *ca.* 400 °C with C–Br bond homolysis followed by reaction with HX (X being Br, Cl or H) to yield $CHClF_2$. At higher temperatures other products arise and complete conversion of $CBrClF_2$ is achieved at *ca.* 600 °C. At temperatures above 850 °C complete dehalogenation to mainly methane (yield 80%) is attained. In the temperature range 450–550 °C the (pseudo) first-order rate constant for the overall reaction (F) was found to obey: $\log (k_F/s^{-1}) = (9.4 \pm 1.5) - (150 \pm 25)\ \mathrm{kJ\ mol^{-1}}/2.303RT$.

The thermolysis of $CBrClF_2$ was also studied using an excess of 2-phenylpropane (cumene) as a radical scavenger, resulting in the following Arrhenius expression for reaction (G): $\log (k_G/s^{-1}) = (15.1 \pm 0.5) - (262 \pm 9)\ \mathrm{kJ\ mol^{-1}}/2.303RT$. From these parameters the bond dissociation energy for the C–Br bond in $CBrClF_2$ was calculated to be 268 ± 8 kJ mol^{-1}, leading to a heat of formation of the $^\bullet CClF_2$ radical of −279 ± 17 kJ mol^{-1}. Kinetic analysis and separate experiments with H_2O_2 as an initiator for making $H^\bullet$ showed that attack by $H^\bullet$ is the main route for decomposition of $CBrClF_2$. At temperatures higher than 500 °C HBr rather than H_2 acts as a hydrogen transfer agent resulting in a fast radical chain (reactions G and L–O) with the observed Arrhenius parameters as a consequence.

Perhalogenated methanes such as chlorofluorocarbons (CFCs) and halons (bromine containing compounds) are, because of their chemical stability and desirable thermophysical properties, widely used as refrigerants, solvents, blowing agents, propellants, cleaning agents and fire extinguishers. In most of these applications large amounts are released into the atmosphere. Due to their long tropospheric lifetimes[1] CFCs and halons diffuse into the stratosphere where chlorine and/or bromine atoms—which act as catalysts to decompose ozone—are released through photolysis. At this moment several CFCs are being replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These hydrogen containing halocarbons have physical properties similar to the CFCs but their tropospheric lifetimes are much shorter because of their susceptibility to hydrogen abstraction by hydroxyl radicals.

Large amounts of residues of CFCs and halons still exist and may be destroyed or converted into less harmful compounds like HCFCs. Incineration of halogenated waste has the drawback of formation of dioxins[2,3] and, further, is a remarkable option for flame retardants and fire extinguishers. We have found that pyrolysis in an atmosphere of hydrogen [*i.e.* thermal hydrodehalogenation (THD)] is a very useful approach.[4] A wide variety of compounds including CH_2Cl_2, CH_2Br_2, (poly)chlorobenzenes and polychlorinated biphenyls (PCBs)[5] can thus be dealt with, resulting in the formation of hydrocarbons and HX. Both full and partial conversions (leading to hydrogen containing halocarbons) can easily be achieved.

For example, the first step in the decomposition of chloromethane (CH_3Cl) in an inert atmosphere (*e.g.* N_2) in an overall process with soot, benzene, C_2H_4 and C_2H_2 as important products is reaction (A).[6] For reaction (A), between

$$CH_3Cl \longrightarrow {}^\bullet CH_3 + Cl^\bullet \qquad \text{(A)}$$

650 and 800 °C, the Arrhenius parameters [eqn. (1)] have been

$$\log (k_A/s^{-1}) = 15.4 - 349\ \mathrm{kJ\ mol^{-1}}/2.303RT \qquad (1)$$

found.[6] The reported bond dissociation energy (BDE) for the C–Cl bond in CH_3Cl amounts to 354 kJ mol^{-1}.[7] However, when working in an atmosphere of hydrogen, hydrogen atoms will be formed [reactions (B) and (C)] which can attack the substrate

$${}^\bullet CH_3 + H_2 \longrightarrow CH_4 + H^\bullet \qquad \text{(B)}$$

$$Cl^\bullet + H_2 \rightleftharpoons HCl + H^\bullet \qquad \text{(C)}$$

$$H^\bullet + CH_3Cl \longrightarrow {}^\bullet CH_3 + HCl \qquad \text{(D)}$$

$${}^\bullet CH_3 + HCl \longrightarrow CH_4 + Cl^\bullet \qquad \text{(E)}$$

[reaction (D)]. This results in a substantially faster rate of HCl formation, in a much cleaner reaction, and lower Arrhenius parameters for the (overall) disappearance of the substrate.[6] The rate determining step is now (D) with eqn. (2). Together

$$\log k_{ovl}/\mathrm{dm^3\ mol^{-1}\ s^{-1}} = 11.1 - 240\ \mathrm{kJ\ mol^{-1}}/2.303RT \qquad (2)$$

with reactions (E) and (C) a radical chain reaction results which can lead to essentially complete dehalogenation.

The present paper deals with the THD of bromochlorodifluoromethane ($CBrClF_2$) over the temperature range 400–900 °C. To gain more information on mechanisms, the thermolysis of $CBrClF_2$ in a large excess of 2-phenylpropane (cumene) and reactions of $CBrClF_2$ with hydrogen atoms, have also been studied. The ultimate goal is to understand pertinent reactions thoroughly enough so that the overall process eventually can be manipulated in a desired way. Therefore, attention has been focussed on products, kinetics and mechanisms.

Experimental

The set-up in which all THD experiments were carried out is schematically drawn in Fig. 1. The alumina plug flow reactor

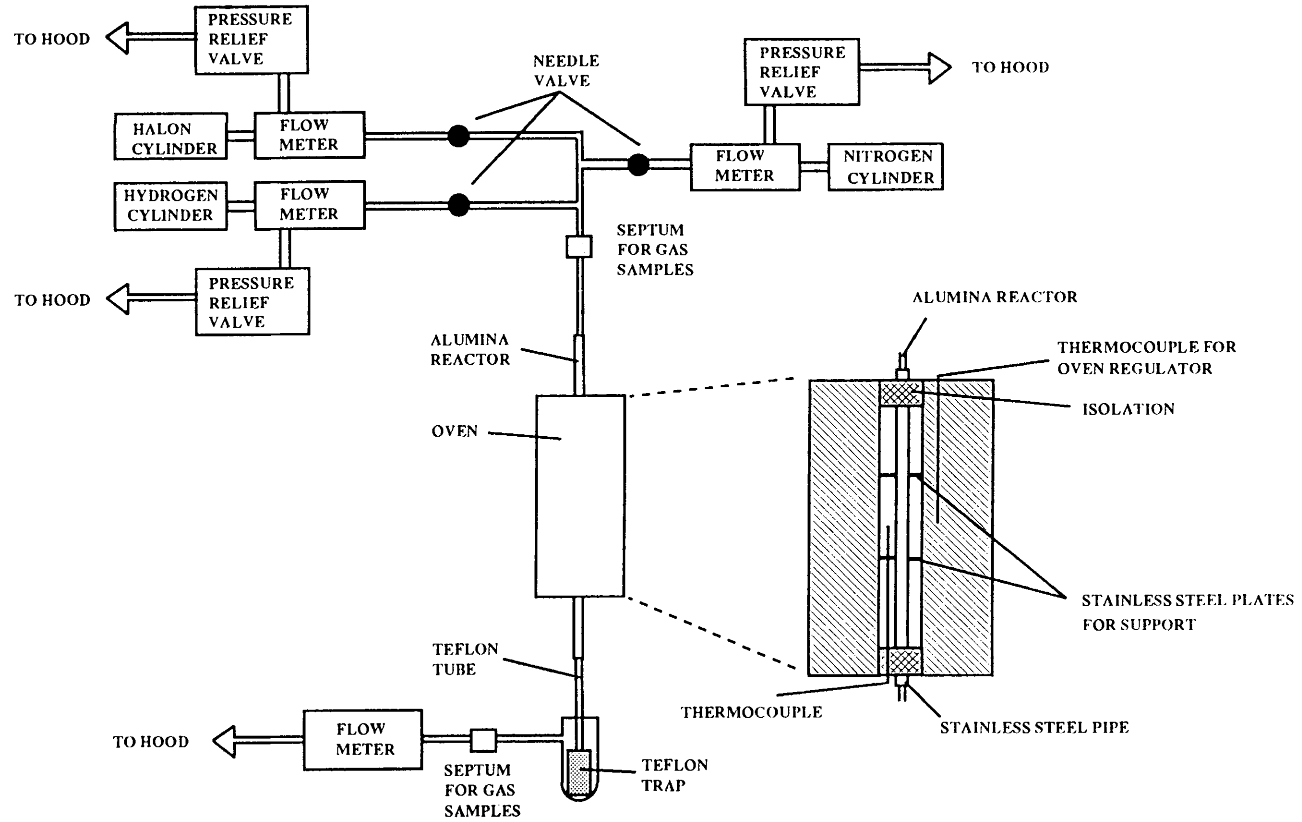

Fig. 1 Schematic drawing (and detail) of the setup used in the THD experiments

(diameter: 0.48 cm; effective volume: 7.26 cm^3) was surrounded by a specially isolated electrically heated furnace controlled by a RKC (model REX-F9) temperature regulator. The temperature was measured by a chromel-alumel thermocouple situated at the middle of the furnace close to the reactor wall. The reactor exit was connected to a teflon tube which led to a teflon trap filled with water to collect HBr, HCl and HF.

$CBrClF_2$ was taken from a commercially available fire extinguisher (Ansul Wormald B.V., Lelystad, The Netherlands) and had a purity of 99.5% (checked by GC). Hydrogen and nitrogen were obtained from Air Products (purity 99.995%). All chemicals were used without further purification. Flows were regulated and metered *via* calibrated flowmeters.

Gas samples were taken from the gas stream using a 0.5 cm^3 gas-tight syringe and analyzed immediately. Both intake and exit gases were analyzed by GC/FID (HP 5890A Gas Chromatograph) on a CP-Sil-5CB (50 m × 0.32 mm i.d., column flow 3 cm^3 min^{-1}) capillary column. Column conditions: split (1 : 20) injections, H_2 carrier gas, flow 60 cm^3/min^{-1}, temperature program: -30 °C (5 min), rate A: 10 °C/min^{-1} to 200 °C (0 min), rate B: 20 °C min^{-1} to 280 °C (10 min). Since the molar response factors of the products were unknown, the following method was used to calculate absolute amounts: C_1-compounds containing one halogen were based on peak areas relative to that of methane; C_1-compounds containing two or three halogens were based on peak areas relative to that of $CBrClF_2$. Amounts of halogenated C_2-compounds were calculated in the same manner.* For product identification, a HP 5890A GC coupled to a HP 5790B Mass Selective Detector was used, employing a similar capillary column and helium as a carrier gas. Non-halogenated C_1 and C_2 exit gases were analyzed using a Packard 436A GC equipped with a Carboplot 007 (10 m × 0.53 mm i.d., column flow 10 cm^3/min^{-1}) wide bore column in conjunction with a methanizer and a flame ionization detector. Column conditions: H_2 carrier gas, flow 10 cm^3 min^{-1}, temperature program: 150 °C (1 min), rate 15 °C min^{-1}, final temperature: 250 °C (1 min). Quantification was performed relative to an external standard (Scotty II, can mix 216) containing 1% of CO, CH_4, CO_2, C_2H_2, C_2H_4 and C_2H_6.

After the experiment the content of the water trap was diluted in a volumetric flask. Aliquots were titrated for HBr and HCl with 0.1 mol dm^{-3} $AgNO_3$ using an automated titrator (Mettler DL 25). HF was determined using a fluoride ion selective electrode (Orion Research, model 96–09–00) and four buffered standard solutions containing different concentrations of NaF. The thermolysis of $CBrClF_2$ in a large excess of 2-phenylpropane (cumene) with fluorobenzene as an internal standard was carried out in a quartz reactor (diameter 0.7 cm; effective volume 7.7 cm^3) with nitrogen as a carrier gas. A 10% solution of $CBrClF_2$ in cumene was fed into the reactor using a motor driven syringe (Braun Melsungen AG, 871 222/0). The products were collected in a cold trap (cooled with liquid nitrogen) and analyzed afterwards with capillary GC/FID.

The reactions of $CBrClF_2$ in the presence of hydrogen peroxide (J. T. Baker, 30% in H_2O) and hydrochloric acid (J. T. Baker, 36.5% in H_2O) were studied in a quartz reactor (effective volume 6.9 cm^3) using hydrogen and/or nitrogen as the carrier gas. Hydrogen peroxide or hydrochloric acid were fed using a motor driven syringe. Gas flows were regulated and metered utilizing electronic mass flow controllers (Brooks 5850 TR Series). Gas samples were taken from the gas stream and analyzed as described above. Aliquots of water samples containing hydrogen peroxide were titrated with 0.1 mol dm^{-3} $Na_2S_2O_4$ (after reaction with aqueous KI/H_2SO_4).[8]

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* This method of calculation resulted for most experiments in reasonable carbon and halogen balances, indicating that this simplification (at least for this compound) is allowed.

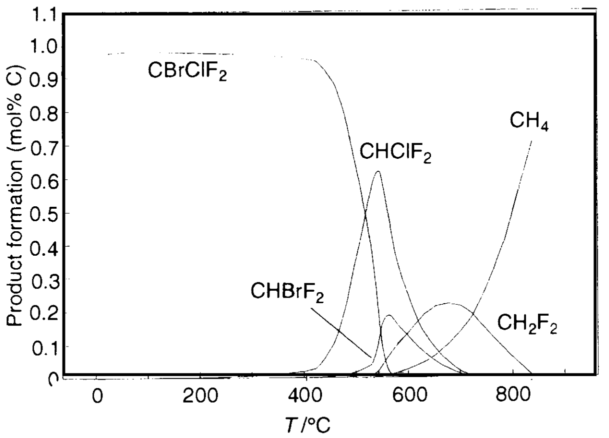

Fig. 2 Formulation of main products as a function of temperature in the THD of $CBrClF_2$

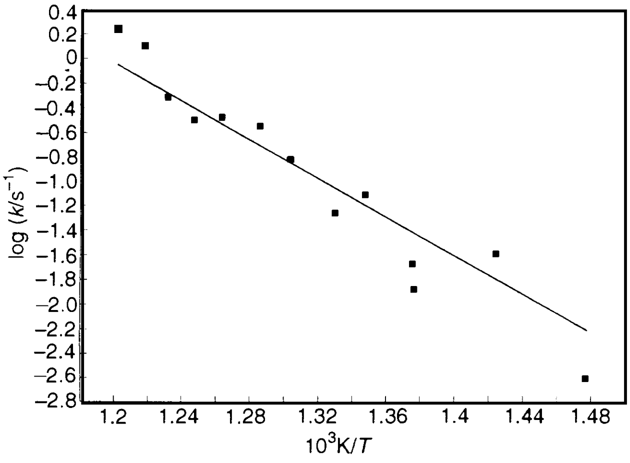

Fig. 3 Arrhenius plot for the THD of $CBrClF_2$, assuming pseudo-first-order kinetics

Results and Discussion

Temperature Variation: Products and Kinetics.—The results of the THD of $CBrClF_2$ between 400 and 900 °C are shown in Fig. 2 and in Table 1. The conversion of $CBrClF_2$ starts at *ca.* 400 °C. The primary product observed is $CHClF_2$ (HCFC-22). At higher temperatures other products such as $CHBrF_2$, CH_2F_2, CH_2BrF, CH_2Cl_2, CH_2Br_2 and CH_3F are formed but until *ca.* 550 °C, $CHClF_2$ remains the major product. The selectivity to $CHClF_2$ is *ca.* 90% at low temperatures and still 50% at a halon conversion of 50% (530 °C). Complete conversion of $CBrClF_2$ is achieved at *ca.* 600 °C but in the temperature range 600–850 °C compounds such as CH_3F, CH_2F_2, $C_2Cl_2F_4$, $C_2H_2F_4$ and $C_2H_3F_3$ can still be detected. Complete dehalogenation of the mixture to mainly methane (80% yield) is achieved only at temperatures above 850 °C.

By using the measured conversion of $CBrClF_2$ (based on product formation) of each experiment, pseudo-first-order reaction rate constants between 450 and 550 °C (20–80% conversion) can be derived if it is assumed that the (excess) H_2 concentration does not change [reaction (F)]. Despite this

$$\mathrm{CBrClF_2} + \mathrm{H_2} \longrightarrow \text{Products} \qquad \text{(F)}$$

simplification, Fig. 3 displays that a reasonable Arrhenius plot for k_F results, obeying eqn. (3).

$$\log k_F/\mathrm{s^{-1}} = (9.4 \pm 1.5) - (150 \pm 25)\,\mathrm{kJ\,mol^{-1}}/2.303RT \qquad (3)$$

Several (consecutive) reactions seem to play an important role since both the experimental pre-exponential factor and the activation energy (E_a) are too low to account for C–Br bond breaking as the rate determining step [reaction (G)].[7,9,10] Furthermore, the overall rate is considerably larger than that based on reaction (G) alone, *vide infra.*

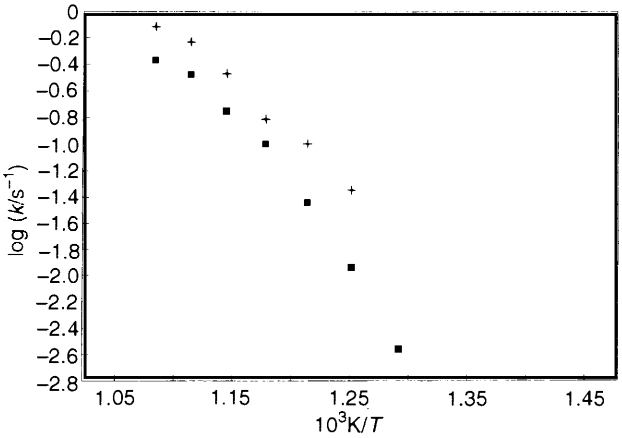

Fig. 4 Arrhenius plot for the thermolysis of $CBrClF_2$ in cumene, assuming plug flow kinetics: ■, product formation; +, substrate disappearance

$$\mathrm{CBrClF_2} \longrightarrow {}^{\bullet}\mathrm{CClF_2} + \mathrm{Br}^{\bullet} \qquad \text{(G)}$$

Thermolysis of $CBrClF_2$ *in Cumene.*—Reaction (G) was studied separately using a large excess of cumene as a radical scavening agent in a nitrogen atmosphere between 425 and 650 °C. After C–Br bond homolysis, both radicals will react with cumene resulting in stable end products ($CHClF_2$, HBr) and (unreactive) cumyl radicals. From the data obtained (Table 2; conversion of the substrate was calculated on basis of product formation and on basis of substrate disappearance relative to the added internal standard) the Arrhenius parameters [eqn. (4)] could be calculated (Fig. 4). For these

$$\log k_G/\mathrm{s^{-1}} = (15.1 \pm 0.5) - (262 \pm 9)\,\mathrm{kJ\,mol^{-1}}/2.303RT \qquad (4)$$

calculations it was assumed that the reaction vessel behaves like an ideal plug flow reactor. The deviation at higher temperatures indicates that it might behave as a tank flow reactor but calculating k_G for a tank flow reactor did not give a better result. This probably means that the deviations at higher temperatures are due to a more complex chemical behaviour of the components. Since the exact reasons for this deviation are as yet unclear, we will not speculate further on this issue.

Ascribing the activation energy [eqn. (4)] to step (G), the C–Br BDE can be derived using eqns. (5) and (6). Using the

$$\Delta H_T^\circ = E_a + RT \qquad (5)$$

$$\Delta H_{298}^\circ = \Delta H_T^\circ + < \Delta C_p^\circ > (298 - T) \qquad (6)$$

tabulated[11] C_p° values for $CBrClF_2$ at 25 and 500 °C, the BDE amounts to 268 ± 8 kJ mol⁻¹. This value is in reasonable agreement with those of earlier studies[7,10] which reported a value of 270 kJ mol⁻¹. With this number we can also derive the heat of formation (ΔH_f°) of the $^{\bullet}CClF_2$ radical. With $\Delta H_f^\circ{}_{298}(CBrClF_2)$ taken as −435 ± 8 kJ mol⁻¹,[11] and that of $Br^{\bullet}$ as 111.7 ± 0.4 kJ mol⁻¹,[12] we can deduce a value of −279 ± 17 kJ mol⁻¹ for $\Delta H_f^\circ{}_{298}({}^{\bullet}CClF_2)$. This value is close to that reported by Miyokawa *et al.* (−279 ± 8 kJ mol⁻¹)[13] and in reasonable agreement with the value advanced by Leyland *et al.* (−269 ± 8 kJ mol⁻¹).[14]

Table 1 Results of the THD of $CBrClF_2$ in the temperature range of 400–900 °C

	T/°C									
	404	429	453	454	469	479	494	505	518	529
Residence time/s	2.5	2.6	2.5	2.7	2.9	2.5	2.7	3.0	2.6	2.5
Intake/mmol h^{-1}										
$CBrClF_2$	17.8	16.3	16.6	15.0	13.0	15.1	12.2	6.6	12.5	12.8
H_2	168.7	156.0	156.8	149.7	133.3	152.4	143.8	61.1	143.1	146.1
Outflow/mmol h^{-1} [a]										
$CBrClF_2$	17.1	15.0	15.7	16.1	10.1	13.3	8.2	3.4	5.6	6.8
CH_4	—	0.002	—	—	0.002	—	0.001	—	0.007	0.006
C_2H_4	—	—	—	—	—	—	—	—	—	—
C_2H_6	—	—	—	—	0.001	—	—	—	0.001	—
CH_3Cl	—	—	—	—	—	—	—	—	—	—
CH_3F	—	—	—	—	—	—	—	—	—	—
CH_3Br	—	—	—	—	—	—	—	—	—	—
CH_2Cl_2	—	—	—	—	—	—	—	—	—	—
CH_2Br_2	—	—	—	—	—	—	—	—	—	—
CH_2F_2	—	—	—	—	—	—	0.03	0.02	0.42	0.04
CH_2BrF	—	—	—	—	—	—	—	—	—	—
$CHClF_2$	0.1	1.0	0.5	0.9	2.5	1.9	3.9	4.4	6.1	7.8
$CHBrF_2$	0.004	0.03	0.02	0.03	0.09	0.07	0.15	0.25	0.32	0.53
$C_2H_3F_3$	—	—	—	—	—	—	—	—	0.5	—
$C_2H_2F_4$	—	—	—	—	—	—	—	—	—	—
$C_2Cl_2F_4$	—	—	—	—	—	—	—	—	—	—
Conversion (%)	1	7	3	6	20	13	33	58	58	55

	T/°C								
	539	548	559	585	670	688	759	773	839
Residence time/s	2.5	3.2	2.6	2.4	2.6	2.6	2.5	2.4	2.5
Intake/mmol h^{-1}									
$CBrClF_2$	12.5	4.5	4.1	5.7	4.1	5.4	4.6	5.0	3.8
H_2	145.4	55.7	69.8	70.1	60.2	57.1	56.7	57.2	53.5
Outflow/mmol h^{-1}									
$CBrClF_2$	3.6	0.06	0.03	0.007	—	—	0.004	0.006	—
CH_4	0.01	0.02	0.01	0.07	0.48	0.09	1.8	1.4	1.9
C_2H_4	—	0.01	0.01	0.004	0.01	0.03	0.2	0.2	0.2
C_2H_6	—	0.01	0.01	0.02	0.04	0.06	0.2	0.2	0.1
CH_3Cl	—	0.02	0.01	0.06	0.12	0.15	0.14	0.14	0.001
CH_3F	—	0.02	0.003	0.03	0.02	0.08	0.12	0.13	—
CH_3Br	—	0.04	0.02	0.19	0.23	0.25	0.09	0.04	—
CH_2Cl_2	—	0.010	0.004	0.03	0.01	0.02	0.003	0.003	—
CH_2Br_2	—	—	—	0.07	0.01	0.001	—	—	—
CH_2F_2	0.07	0.12	0.16	0.51	0.69	2.17	0.74	0.52	0.001
CH_2BrF	—	0.09	0.05	0.28	0.18	0.37	0.03	0.01	—
$CHClF_2$	7.71	2.06	1.60	1.19	0.02	0.06	0.004	0.008	—
$CHBrF_2$	0.57	0.78	0.58	0.67	0.004	0.04	0.003	0.005	—
$C_2H_3F_3$	—	0.007	0.02	0.10	0.45	0.74	0.69	1.04	—
$C_2H_2F_4$	—	0.01	0.05	0.51	0.20	0.61	0.15	0.12	—
$C_2Cl_2F_4$	0.002	0.04	0.04	0.09	0.08	0.12	0.07	0.07	—
Conversion (%)	70	98	99	> 99	> 99	> 99	> 99	> 99	> 99

[a] (—) Denotes below detection limit < 0.001 mmol h^{-1}.

From the parameters of eqn. (4) it can be derived that at 500 °C and a residence time of 2.3 s only 0.5% conversion should occur. In fact, in a hydrogen atmosphere, about 50% is converted (Fig. 5). In hydrogen, therefore, induced decomposition is by far the most important route for disappearance of $CBrClF_2$.

Reaction of $CBrClF_2$ *with Hydrogen Peroxide.*—It is of interest to try to enhance the rate of hydrodehalogenation at modest temperatures by chemically creating 'extra' H-atoms. *A priori*, several approaches can be envisaged such as adding a labile donor of $Cl^•$, using small amounts of oxygen or adding a source of OH radicals. We have chosen to conduct a short series of experiments with added hydrogen peroxide. If heterogeneous (non-radical) decomposition is unimportant, it acts as a source of $^•OH$ (H) and results in the formation of $H^•$(I). As can be seen

$$H_2O_2 \longrightarrow 2\,OH^• \qquad \text{(H)}$$

$$OH^• + H_2 \longrightarrow H_2O + H^• \qquad \text{(I)}$$

from Table 3, in most experiments the ratio $CBrClF_2:H_2O_2:H_2$ was 3 : 1: ≈ 18.

Table 2 Results of the thermolysis of $CBrClF_2$ in cumene between 425 and 650 °C

	T/°C								
	425	451	501	526	551	576	601	625	650
Residence time/s	2.4	2.4	2.6	2.4	2.4	2.6	2.6	2.5	2.4
Intake (%)									
$CBrClF_2$	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Outflow (%)									
$CBrClF_2$	100.0	100.0	99.3	97.3	91.5	76.0	60.2	38.3	28.4
$CHClF_2$	—	—	0.7	2.7	8.5	23.0	37.0	56.3	64.2
$CHBrF_2$	—	—	—	—	—	0.9	2.4	3.7	3.0
CH_2F_2	—	—	—	—	—	0.1	0.4	1.6	4.2
$C_2Cl_2F_4$	—	—	—	—	—	—	—	—	0.1
Conversion (%)[a]	—	—	0.7	2.7	8.5	23.0	37.0	56.3	64.2
Conversion (%)[b]	—	—	—	10.4	22.0	32.8	58.7	76.8	84.4

[a] Conversion based on product ($CHClF_2$) formation. [b] Conversion calculated on basis of substrate disappearance relative to internal standard (fluorobenzene).

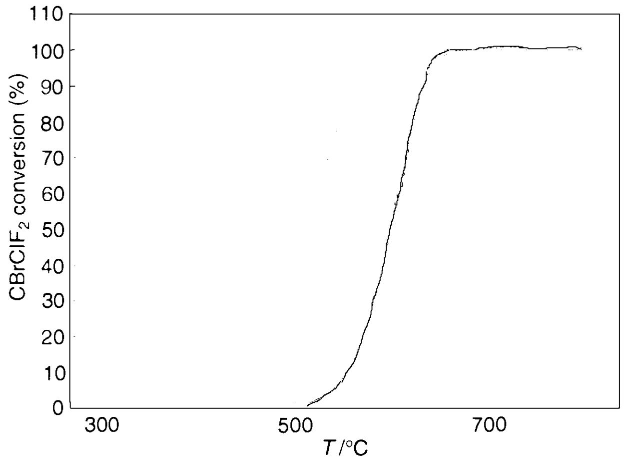

Fig. 5 Differences in conversion between the thermolysis in cumene and the THD of $CBrClF_2$: ·······, THD; ——, thermolysis

The presence of hydrogen peroxide results in higher conversions of the substrate (by a factor of *ca.* two). In the temperature range employed (400–475 °C) C–Br bond breaking only plays a minor role and therefore we can conclude that the products observed ($CHClF_2$, $CHBrF_2$, CH_2F_2 and $C_2Cl_2F_4$) are the result of induced decomposition of the substrate (*i.e.* attack of H-atoms). In these experiments the $CHClF_2$:$CHBrF_2$ ratio remains constant (13.5) over the investigated temperature range but is lower than in the 'normal' THD experiments where the ratio is *ca.* 16. Reaction of OH radicals with $CHClF_2$ is slower than the corresponding reaction with H_2 by a factor of *ca.* three and should not therefore play an important role. It is also unlikely that higher $H^{\bullet}$ concentrations will result in a lower selectivity for bromine abstraction *vs.* chlorine abstraction. The observed selectivities cannot be explained on basis of the exothermicities, ΔH_r, for reactions (J) and (K). The

$$H^{\bullet} + CBrClF_2 \longrightarrow HBr + {}^{\bullet}CClF_2 \quad \Delta H_r = -100\ \text{kJ mol}^{-1} \qquad (J)$$

$$H^{\bullet} + CBrClF_2 \longrightarrow HCl + {}^{\bullet}CBrF_2 \quad \Delta H_r = -113\ \text{kJ mol}^{-1} \qquad (K)$$

$\Delta H_f({}^{\bullet}CBrF_2)$ at 298 K needs to be estimated in order to compute the reaction enthalpy of reaction (K). The $\Delta H_f({}^{\bullet}CClF_2)$ is *ca.* -280 kJ mol^{-1}, while for ${}^{\bullet}CClH_2$ radical a value of 130 kJ mol^{-1} has been suggested;[15a] if this increment also holds for ${}^{\bullet}CBrH_2 \rightarrow {}^{\bullet}CBrF_2$ then the $\Delta H_f({}^{\bullet}CBrF_2)$ amounts to *ca.* -239 kJ mol^{-1}. Within the uncertainty both processes show a similar exothermicity.

From literature data[15] it can be derived that bromine abstraction by $H^{\bullet}$ from CH_3Br is faster than chlorine abstraction from CH_3Cl. The difference in activation energy amounts to 13–17 kJ mol^{-1}. If this energy gap also holds for the internal competition in $CBrClF_2$ then, over the temperature range employed, a selectivity (k_J/k_K) of *ca.* 13 can be calculated which is close to the measured value.

Mechanistic Aspects.—The data obtained from experiments in H_2 and in cumene show that in the low temperature range (400–500 °C) rupture of the C–Br bond (G) initiates a radical chain (L–O).

$$CBrClF_2 \longrightarrow {}^{\bullet}CClF_2 + Br^{\bullet} \qquad (G)$$

$${}^{\bullet}CClF_2 + H_2 \longrightarrow CHClF_2 + H^{\bullet} \qquad (L)$$

$$Br^{\bullet} + H_2 \longrightarrow HBr + H^{\bullet} \qquad (M)$$

$${}^{\bullet}CClF_2 + HBr \longrightarrow CHClF_2 + Br^{\bullet} \qquad (N)$$

$$H^{\bullet} + CBrClF_2 \longrightarrow HBr + {}^{\bullet}CClF_2 \qquad (O)$$

At 530 °C (*ca.* 50% conversion) k_F, for the overall reaction, is calculated to be *ca.* 0.4 s^{-1} [eqn. (3)]. As stated before, reaction (G) plays only a minor role: $k_G \approx 0.01$ s^{-1}. From these results the chain length (as defined by v_F/v_G) of this process is calculated to be *ca.* 40. Under these conditions we should expect a low amount of C_2-compounds, products of radical–radical recombinations, to be formed. This is indeed the case: at low temperatures (until 550 °C) less than 5% of the products are termination products (C_2H_4, C_2H_6, $C_2H_3F_3$, $C_2H_2F_4$ and $C_2Cl_2F_4$). In the temperature range 550–900 °C their yield rises to *ca.* 40% (775 °C). Accordingly, at the high temperature side of this study reaction (G) is relatively more important.

As can be seen from Table 4, reaction (O) is the major chain propagating step. So, at 530 °C, the overall rate implies that $k_O[H^{\bullet}] = 0.4$ s^{-1}. At that temperature $k_O = 4.6 \times 10^8$ dm^3 mol^{-1} s^{-1} (Table 4; ref. 25). The actual H-atom concentration is therefore *ca.* 9×10^{-10} mol dm^{-3}, much larger than expected if $[H^{\bullet}]$ would be governed by equilibrium (P) since, under these

$$H_2 \rightleftharpoons 2H^{\bullet} \qquad (P)$$

Table 3 Results of the experiments of $CBrClF_2$ with added hydrogen peroxide

	T/°C													
	402	402	422	422	448	448	474	474	460	460	434	437	474	473
Residence time/s	2.5	2.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Intake/mmol h^{-1}														
$CBrClF_2$	24.9	24.9	50.0	50.0	50.0	50.0	44.9	44.9	50.0	50.0	50.0	50.0	50.0	50.0
H_2	126.6	126.6	325.6	325.6	307.1	307.1	297.9	297.9	302.5	302.5	316.4	316.4	293.2	0.0
N_2	—	30.0	59.7	—	59.7	—	—	59.7	59.7	—	59.7	—	—	292.8
H_2O_2	8.3	—	—	16.5	—	16.5	16.5	—	—	16.5	—	16.5	16.5	16.5
H_2O	22.2	—	—	44.4	—	44.4	44.4	—	—	44.4	—	44.4	44.4	44.4
Outflow/mmol h^{-1}														
$CBrClF_2$	21.0	23.4	46.2	43.3	47.2	44.3	33.1	37.8	46.8	42.1	45.5	49.3	42.7	49.8
$CHClF_2$	0.14	0.22	0.49	0.79	1.41	2.56	4.65	3.17	2.15	2.89	0.71	0.58	4.11	0.02
$CHBrF_2$	—	—	0.04	0.06	0.09	0.18	0.33	0.21	0.13	0.21	0.04	0.04	0.30	—
CH_2F_2	—	—	—	—	0.05	—	0.03	0.11	0.08	0.03	0.03	0.00	0.02	—
$C_2Cl_2F_4$	—	—	0.06	—	—	—	0.03	0.03	0.01	—	—	—		—
Conversions (%)														
$CBrClF_2$ (GC)	15.7	6.0	7.7	13.5	5.6	11.4	26.3	15.7	6.4	15.8	9.0	1.4	14.6	0.4
H_2O_2 (titration)	45.9	—	—	73.5	—	95.3	91.3	—	—	97.6	—	96.7	*a*	100.0
C-balance (%)	85	95	94	88	98	94	85	92	98	91	93	> 99	94	> 99
$CHClF_2/CHBrF_2$	—	—	12.5	12.8	16.0	13.9	13.9	14.9	16.4	13.6	16.9	13.0	13.7	—

[a] Not determined.

Table 4 Arrhenius parameters and rate constants at 530 °C[a] for reactions (G, L–O)

Reaction	log A	E_a	k	Ref.
G	15.3	265	1.18×10^{-2}	*b*
L	8.9	40	2.06×10^{6}	*c*
M	11.2	80	9.43×10^{5}	*d*
N	8.4	11	5.05×10^{7}	*e*
O	11.2	39	4.55×10^{8}	*f*

[a] Units: s^{-1} dm^3 mol^{-1} and kJ mol^{-1}. [b] This work. [c] Reaction referred to is: $^{\bullet}CF_3 + H_2 \rightarrow CHF_3 + H^{\bullet}$, ref. 24. [d] Ref. 25. [e] Reaction referred to is: $^{\bullet}CF_3 + HBr \rightarrow CHF_3 + Br^{\bullet}$, ref. 26. [f] Reaction referred to is: $H^{\bullet} + CF_3Br \rightarrow HBr + {}^{\bullet}CH_3$, ref. 25.

circumstances, this would result in a H-atom concentration o4 *ca.* 10^{-13} mol dm^{-3}. After C–Br bond homolysis the $^{\bullet}CClF_2$ radical will abstract hydrogen from a suitable H-donor molecule. At low temperatures this will be H_2 because of its excess, but with increasing temperature more HBr will be formed (M, O) and HBr can now compete with H_2 (reaction N *vs.* L). HBr is known to be a very good hydrogen transfer agent; reactions with alkyl radicals are very fast and the activation energies are negligible, if not negative.[16–20] However, replacing H in CH_3 by halogen, as in CF_3, results in slower H-transfer reactions with HBr [for the reaction of $^{\bullet}CF_3$ with HBr the rate constant at 530 °C is 5×10^7 dm^3 mol^{-1} s^{-1} (ref. 26); *cf.* reaction (N) Table 4]. Nevertheless, $^{\bullet}CF_3$ still reacts *ca.* 25 times faster with HBr than with H_2 (Table 4) at that temperature. Consequently, H-transfer to $^{\bullet}CClF_2$ will be dominated by (N) already at modest degrees of conversion.

H-Transfer can also take place with HCl. Reactions (L) and (Q) have nearly the same heat of reaction, but studies in our laboratory[6,21] prove that reaction (Q) is faster than reaction (L).

$$^{\bullet}CClF_2 + H_2 \longrightarrow CHClF_2 + H^{\bullet} \quad \Delta H_r = +31 \text{ kJ mol}^{-1} \quad \text{(L)}$$

$$^{\bullet}CClF_2 + HBr \longrightarrow CHClF_2 + Br^{\bullet} \quad \Delta H_r = -38 \text{ kJ mol}^{-1} \quad \text{(N)}$$

$$^{\bullet}CClF_2 + HCl \longrightarrow CHClF_2 + Cl^{\bullet} \quad \Delta H_r = +26 \text{ kJ mol}^{-1} \quad \text{(Q)}$$

Reaction of $CBrClF_2$ *with Hydrochloric Acid*.—Homolysis of the C–Cl bond in $CBrClF_2$ is negligibly slow, so the formation of $CHBrF_2$ (which also reaches a maximum at *ca.* 530 °C) must proceed differently. Two pathways can be distinguished: (i) Cl abstraction from the substrate by $H^{\bullet}$ (R) and subsequent

$$H^{\bullet} + CBrClF_2 \longrightarrow HCl + {}^{\bullet}CBrF_2 \quad \text{(R)}$$

hydrogenation (S) by either H_2, HBr or HCl; (ii) elimination of

$$^{\bullet}CBrF_2 + HX \longrightarrow CHBrF_2 + X^{\bullet} \quad \text{(S)}$$

HCl from $CHClF_2$ (T) and subsequent addition of HBr to difluorocarbene, $:CF_2$ (U). Reactions (T), (–T), (U) and (–U)

$$CHClF_2 \rightleftharpoons HCl + :CF_2 \quad \text{(T, –T)}$$

$$HBr + :CF_2 \rightleftharpoons CHBrF_2 \quad \text{(U, –U)}$$

have been studied by Simmons and co-workers.[22,23] The observed rate parameters are given in Table 5, allowing calculation of rates and equilibria at 530 °C. An important feature here is the ratio HCl : HBr. This ratio can be calculated using eqn. (7). Under 'normal' THD conditions the ratio $CHClF_2 : CHBrF_2$ is *ca.* 10. Using the k-values given in Table 5, a value of 5.2 for the HCl : HBr ratio is obtained. Note that this is only true when $CHClF_2$ and $CHBrF_2$ are formed *via* reactions (T), (–T), (U) and (–U). The measured (outflow) HCl : HBr ratio is *ca.* 1 at high temperatures but small at lower temperatures (0.086 at 530 °C). This is reasonable since most of the $CHClF_2$ will be formed *via* reactions (L) and (N).

Table 5 Kinetic data[a] for reactions (T, −T, U, −U)

Reaction	log *A*	E_a	*k* (530 °C)	log *K*
T	12.6	221	1.70×10^{-2}	
−T	8.33	51	1.07×10^{5}	−6.80
U	8.33	40	5.21×10^{5}	
−U	14.33	233	1.58×10^{-1}	−6.52

[a] Units: s^{-1}, $dm^3\ mol^{-1}\ s^{-1}$ and $kJ\ mol^{-1}$.

Table 6 Results of the experiments of $CBrClF_2$ with added hydrogen chloride

	T/°C		
	529	529	529
Residence time/s	1.0	1.0	1.0
Intake/mmol h^{-1}			
$CBrClF_2$	15.1	15.1	15.1
H_2	38.6	38.6	362.7
N_2	—	322.6	0.0
NCl	71.4	—	0.0
H_2O	251.7	—	0.0
Outflow/mmol h^{-1}			
$CBrClF_2$	10.2	12.6	6.6
$CHClF_2$	4.61	1.63	5.97
$CHBrF_2$	0.04	0.27	0.68
CH_2F_2	0.06	0.27	0.38
$C_2Cl_2F_4$	0.04	0.02	0.01
Conversion (%)			
$CBrClF_2$	32.4	16.4	56.0
C-balance (%)	99.3	98.3	90.7
$CHClF_2/CHBrF_2$	111.2	5.9	8.8

$$(k_T/k_{-T}) \times (k_U/k_{-U}) = [HCl]/[HBr] \times [CHBrF_2]/[CHClF_2] \quad (7)$$

To determine how $CHBrF_2$ is actually formed, the THD of $CBrClF_2$ was studied in the presence of HCl (and H_2O) and H_2 at 530 °C (Table 6). In order to suppress reaction (U) [and stimulate reaction (−T)], a two-fold excess of HCl (over H_2) was used. Analysis of the products showed that the $CHClF_2:CHBrF_2$ ratio is raised from *ca.* 10 under 'normal' THD conditions to *ca.* 100 with the above mentioned amount of added HCl. Therefore we conclude that the main route to $CHBrF_2$ formation is *via* reactions (T) and (U).

Products arising at higher temperatures, such as CH_2F_2, CH_3F and CH_4 can be explained by abstraction of bromine, chlorine and fluorine from $CHBrF_2$, $CHClF_2$, CH_2F_2 and CH_3F respectively by H˙ and subsequent hydrogenation by HX (X being Br, Cl or H). Furthermore, the presence of (halogenated) ethanes in the product mixture proves that radical–radical recombinations (V–X) also occur.

$$\dot{C}ClF_2 + \dot{C}ClF_2 \longrightarrow C_2Cl_2F_4 \quad (V)$$

$$\dot{C}HF_2 + \dot{C}HF_2 \longrightarrow C_2H_2F_4 \quad (W)$$

$$\dot{C}HF_2 + \dot{C}H_2F \longrightarrow C_2H_3F_3 \quad (X)$$

At higher temperatures, C_2H_6 and C_2H_4 are also formed. Ethane will be the result of the recombination of two methyl radicals (Y).

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6 \quad (Y)$$

Elimination of H_2 (Z)—a two step radical process *via* ethyl—

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \quad (Z)$$

would then result in the formation of ethylene.

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