Interconversion of Chlorofluorocarbons in Plasmas

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Chlorofluorocarbons undergo interconversion during destruction in an argon arc plasma, so that, for example, in the exhaust gas from destruction of CCl_2F_2, $CClF_3$ is found to be the major residual ozone depleting substance: as electron capture detectors are 10^4 times less sensitive for $CClF_3$, compared with CCl_2F_2, although these gases have the same ozone depleting potential, analysis of exhaust from destruction of chlorofluorocarbons is therefore not a trivial matter of determining only the level of input chlorofluorocarbon remaining.

Destruction of chlorofluorocarbon (CFC) and chlorinated methane wastes in thermal plasmas to levels greater than the 99.99% required by the Montreal Protocol[1] has been reported.[2,3] In the plasma device[4] used in the experiments described here a commercial plasma torch[5] is used to strike an arc in a stream of argon (45 l min^{-1}) at atmospheric pressure. The CFC and the oxygen carrier gas are added at an injection manifold, and the mixture of plasma, CFC, oxygen, and reaction products flows in a flight tube to a water spray quench, which freezes the composition of products before entering an alkaline scrubber at the end of the device. The exhaust gas from the scrubber is sampled and analysed on-line every four minutes during destruction experiments by means of a Varian Saturn 2 gas chromatograph/mass spectrometer (GC/MS). Substances such as CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $CClF_3$ (CFC-13) and $CClF_2H$ (CFC-22), on elution from the GC, are identified by mass spectroscopy and quantified by monitoring the ions of m/z = 85 ($CClF_2^+$) and m/z = 101 (CCl_2F^+) in the mass spectrum. Calibration of the GC/MS response is done with a standard mixture of 75 ppm CFC-12 in argon. Results are expressed as an ozone depleting substance (ODS) residual, where ODS residual = 10^6 (ODS concentration in exhaust/ODS concentration in input gas) (volume flow exhaust/volume flow input gas).

The Montreal Protocol level of 99.99% destruction equals a total ODS residual in the exhaust gas of 100. Three typical results of CFC waste destruction experiments are given in Table 1, which shows the total ODS residual and the component partial residuals of CFC-11, CFC-12, CFC-13 and CFC-22.

These results clearly illustrate the importance of reporting performance in CFC destruction technology in terms of total ODS residual, not in terms of the percentage destruction of the input CFC. The destruction level estimated for CFC-12 in particular is quite different when expressed as percentage input CFC destroyed (99.99995%, equivalent to the partial residual of 0.5 in the example given in Table 1) than as total residual ODS (63 in the example, which translates to 99.9937% ODS destruction). CFC-12 also gives the most extreme example of interconversion, in that the residual ODS is almost entirely CFC-13, which along with CFC-12 and CFC-11, has the rating of 1.0 in stratospheric ozone destruction potential.[1] Sekiguchi *et al.*[3] used gas chromatography to analyse the exhaust gas from their plasma destruction experiment on CFC-12. They gave only the qualitative result that no CFC-12 had been detected, and did not indicate whether they had analysed for other CFC products.

The disproportionation of CFCs is known to occur over an aluminium chloride catalyst[6] but in homogeneous reactions CFC-12 is known to be stable to 500 °C.[7] The tendency for CFCs to interconvert at higher temperatures during pyrolysis or combustion is a consequence of reactions which have been much investigated in recent years, particularly in connection with the chemistry of stratospheric ozone. The decomposition of CFC-12, for example, may be described by a reaction scheme which begins with dissociation [eqn. (1)]

$$CCl_2F_2 \rightarrow CClF_2\cdot + Cl\cdot \qquad (1)$$

Further dissociation of $CClF_2\cdot$ yields CF_2: and dissociation of the oxygen carrier gas gives oxygen atoms. Reactions (2) and (3)

$$CClF_2\cdot + O\cdot \rightarrow CF_2O + Cl\cdot \qquad (2)$$

$$CF_2: + O\cdot \rightarrow CO + 2\,F\cdot \qquad (3)$$

then yield chlorine and fluorine atoms and these may then recombine with CF_2: to yield alternative CFCs in a series of three-body reactions such as (4) and (5)

$$CF_2: + F\cdot + M \rightarrow CF_3\cdot + M \qquad (4)$$

$$CF_3\cdot + Cl\cdot + M \rightarrow CClF_3 + M \qquad (5)$$

The reaction scheme given by Sekiguchi *et al.*[3] to describe the chemical kinetics of their plasma destruction technique for CCl_2F_2 with H_2 and O_2 in argon did not allow for recombination reactions such as eqns. (4) and (5). A consequence of these reactions is that, not only is $CClF_3$ formed from CCl_2F_2, in amounts which can dominate the residual in the plasma exhaust gas, but also a major product of the decomposition is CF_4, an inert gas which is not an ozone depleting substance. Our complete reaction scheme for the decomposition of CFC-12 is much longer than that of Sekiguchi *et al.*[3] and we will not document it here beyond indicating that typical data used for eqns. (1)–(5) are given in refs. 8–12.

Given the flows of argon, CFC-12 and oxygen, and the efficiency of the plasma torch (approx. 50%), a mixing temperature, T_m = 1835 °C was calculated for the CFC-12 result given in Table 1, by means of the CSIRO Thermochemistry System of Turnbull and Wadsley.[13] A simulation of the kinetic scheme for CFC-12 at this temperature for 2 ms., by means of the Larkin[14] chemical kinetics program gave the production curve for $CClF_3$ from CFC-12 shown in Fig. 1. The result shows that substantial conversion of CFC-12 into CFC-13 may be expected in the mixing region of the device under these conditions. A reaction time of 2 ms is longer than the expected residence time in the mixing region, and the temperature experienced by the CFC during a destruction experiment should fall by about 1000 K between mixing region and quench so that the rate of disappearance of CFC-13 at reaction times greater

Table 1 Experimental residuals of ODS from plasma destruction of CFCs

CFC (l min^{-1})	O_2 (l min^{-1})	Power (kW)	CCl_3F Residual	CCl_2F_2 Residual	$CClF_3$ Residual	$CClF_2H$ Residual	Total ODS Residual
11 (31)	34	30	60	1	34	0	95
12 (27)	30	22	0	0.5	62	0	63
22 (45)	45	15	0	1	36	12	49

than 1 ms shown in Fig. 1 would not in fact be achieved. A comprehensive simulation of the reaction of CFC-12 in the device requires more detailed modelling of the hydrodynamic and heat flows, which is in progress.

CFC-13 and CFC-12 are readily detected in GC/MS by monitoring the ion $CClF_2^+$ in the mass spectrum, but for GC analysis without mass spectroscopy, the electron capture detector (ECD) which is commonly used in GC analysis of halogenated materials, is a factor of 10^4 less sensitive for CFC-13 than for CFC-12,[15] making CFC-13 the more difficult product to detect during on-line monitoring of the destruction process by GC/ECD. Other methods of destroying CFCs may also cause interconversion and generate CFC-13 by recombination reactions. Analytical procedures for on-line monitoring of CFC destruction technologies must therefore be designed to permit detection of CFC-13 at lower than the 99.99% destruction level stipulated by the Montreal Protocol.

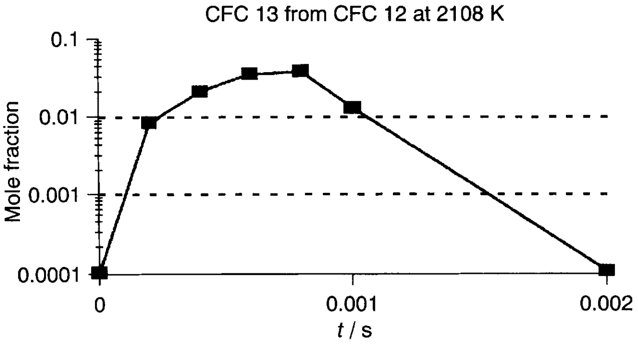

Fig. 1 Production of $CClF_3$ (■) from CCl_2F_2 in kinetic simulation of argon plasma

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