DECOMPOSITION OF HALOGENATED HYDROCARBONS IN SILENT ELECTRIC DISCHARGE

Katalin A. Fõglein and János Szépvölgyi

Research Laboratory of Materials and Environmental Chemistry,
Chemical Research Center, Hungarian Academy of Sciences,
H-1025 Budapest, Pusztaszeri út 59-67. Hungary

Abstract

Decomposition of chlorofluorocarbons (CFCs) was studied in silent electric discharge (SED). The investigations aimed at having a deeper insight into the decomposition mechanism of CCl_4, $CHCl_3$, $CFCl_3$, CF_2Cl_2 and CF_3Cl as models. Particular compounds were destructed in the presence of argon and oxygen, respectively. The reaction products were analyzed by gas chromatography (GC), UV spectrophotometry and FT-IR spectroscopy. It was found that in oxidative conditions the chlorinated and/or fluorinated methanes could be decomposed to harmless products in SED.

Introduction

Chlorofluorocarbons (CFCs) such as CCl_4 (CFC 10), $CFCl_3$ (CFC 11) and CF_2Cl_2 (CFC 12) have been in widespread use previously in a number of applications, including refrigeration fluids, cleaning and foam blowing agents. These compounds are chemically inert in the troposphere. However, when transported into the stratosphere they are subjected to photolysis, which leads to the formation of ozone depleting Cl radicals.

To protect the stratospheric ozone layer and to reduce ozone depletion in the Antarctic, the Montreal Protocol (1987) and its revisions (London 1990, Copenhagen 1992, Montreal 1997) called for a phase out of CFCs and destruction of their reserves. As a result, at least partial replacement of the CFCs by hydrochloro-fluorocarbons (HCFCs) and/or hydro-fluorocarbons (HFCs) is being actively considered and implemented. Special attention is devoted to the CFC degradation, as well [1].

Compounds containing C-H bonds such as HFCs, HCFCs and hydrocarbons (HCs) react with hydroxyl (OH) radical in the troposphere. This reaction limits their atmospheric lifetimes to a few years (compared to 100 year for the CFCs) and minimizes their transport into the stratosphere. Nowadays, the tropospheric chemistry of the HFCs and HCFCs, the degradation pathway and the products formed in the troposphere are investigated intensively [2-9]. However, few data have been reported on the decomposition kinetics of CFCs, HCFCs, HCs and HFCs in the gas-phase. Our aim was to have an insight into these processes.

The silent electric discharge (SED) can be used to decompose the above compounds. Decomposition in SED is based on the impact of electrons accelerated by an electric field with the target molecules. SED can be regarded as a non-equilibrium plasma: temperature of the gas phase is near to room temperature, while the temperature of electrons is higher than 10^4K i.e. 200 kJ mol^{-1} [10]. It exceeds the activation energy of conventional chemical reactions, which is near to 100 kJ mol^{-1}.

Experimental

Three static, cylindrical reactors with double glass walls were used for the investigations. The reactors were filled up with a gas mixture of given pressure and composition. The measurements were carried out at a voltage of 11,000 V and temperature of 298K. The reaction products were analyzed in the gas phase by UV spectrophotometry (HP 8452-A Diode Array) and by FT-IR spectroscopy (BioRad FTS65A/896; detected by DTGS).

Results and Discussion

CCl_4-Ar System. After switching on the mains $CCl_3^\cdot$ and $Cl^\cdot$ are formed due to the collision of electrons with CCl_4. Argon atoms can take away the energy released in the process. The radicals react with each other giving C_2Cl_6 and Cl_2 as recombination products.

$CHCl_3$-Ar System. The electrons could cleave the C-H bond more easily as compared to the C-Cl bond. Thus, $CHCl_3$ decomposed with a higher rate than CCl_4. The products measured by GC-UV method include CCl_4, $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, C_2Cl_6, $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4, $C_3H_3Cl_5$, $C_3H_2Cl_6$, C_3HCl_7, C_3Cl_8 and HCl. No Cl_2 was detected in this system. Though the mass balance was more than 94 and 98 % for carbon and chlorine, respectively, it could be supposed that chlorinated butanes were formed in small quantities.

$CFCl_3$-Ar System. The electron energy in our system is close to the dissociation energy of C-F bond. In principle, the electrons can break C-F bond in $CFCl_3$. However, the binding energy of C-Cl bond is lower as compared to that of C-F bond, and mostly the former one is cleaved. Radicals formed due to the cleavage of C-Cl bond react with Cl from the gas phase. The intermediates then disproportionate by halogen transfer reactions, and halogen-containing methane derivatives (CCl_4, CF_2Cl_2, CF_3Cl) and chlorine are formed. No fluorine gas was detected in the system i.e. free $F^\cdot$ radicals were not formed. However, the fluorine atom could migrate, and CF_2Cl_2 and CF_3Cl were formed in halogen transfer reactions. Chlorofluoro-ethanes such as CFC 112 ($C_2Cl_4F_2$) were not detected.

CF_2Cl_2-Ar System. In the CF_2Cl_2-Ar system CF_2Cl_2 is mainly formed in halogen transfer reactions. CF_2Cl_2 is then transformed to CF_3Cl and CF_4, which contain a large amount of fluorine and do not react with ozone. About 60% of CF_2Cl_2 was converted into more fluorinated compounds. Radicals formed in the electron collision reactions were recombined by reacting with Cl from the gas phase. Although CCl_4 and $CFCl_3$ were produced in this system as well, these compounds could be converted to $CFCl_3$, CF_2Cl_2 and CF_3Cl. The probability by which CF_4 picks up chlorine atoms from the gas phase is almost zero. Thus, the state of equilibrium cannot be reached due to the presence of CF_4. Fluorine gas was not detected as product. The lowest conversion rate was measured in this system. CFC 114 ($C_2Cl_2F_4$), the expectable chlorofluoro-ethane product was not formed.

CF_3Cl-Ar System. The products of this system are also halogenated methanes such as $CFCl_3$, CF_2Cl_2, CF_4 and chlorine, respectively. Decomposition of CF_3Cl is slower than that of CCl_4 and $CHCl_3$, but it is faster as compared to the decomposition of CF_2Cl_2. Decomposition of CF_3Cl is slower than the decomposition of $CFCl_3$, as well, due to the differences in the binding energies of C-F and C-Cl bonds. Recombination of the radicals gives halogenated methanes in all CFC-Ar systems. Halogenated ethanes do not form, because the CFCs are more stable than CCl_4 and $CHCl_3$. CFC 116 (C_2F_6) was not measured in the given case. The general reaction mechanism is described in Table 1 [11-12].

CCl_4-O_2 System. Radicals such as $CCl_3^\cdot$ and $Cl^\cdot$ were formed in the reaction of CCl_4 with electrons. The haloalkyl radicals react rapidly with O_2 to yield haloalkyl peroxy radicals.

Self-reaction of the latter leads to the formation of haloalkoxy radicals. Thus, decomposition of CCl_4 in the presence of oxygen produces alkoxy radicals. These radicals then can undergo unimolecular decomposition via C-Cl bond scission or via O- or Cl-elimination leading to the formation of phosgene. Finally the phosgene decomposes to carbon dioxide and chlorine.

$CHCl_3$-O_2 System. The products of this mixture are similar as above. The intermediates are carbon monoxide and hydrogen chloride, which subsequently decompose to phosgene, carbon dioxide, chlorine and waters. The elementary reaction steps are also the same as above. However, in the $CHCl_3$-O_2 case the H radical can react with the oxygen molecule or atom and $HO_2^{\cdot}$ or $OH^{\cdot}$ radicals are formed. The $OH^{\cdot}$ radical can cleave the C-Cl bond of phosgene, and in the self-reaction of carbonil monochloride radical, carbon monoxide and chlorine radical are produced.

CH_2Cl_2-O_2 System. The product distribution in this system was similar to that of in the $CHCl_3$-O_2 system. Carbon monoxide was detected as intermediate in this mixture, as well. It refers to the important role of $OH^{\cdot}$ radical in the revelation of carbon monoxide. The $CCl_4 \leftarrow CHCl_3 \leftrightarrow \mathbf{CH_2Cl_2} \leftrightarrow CH_3Cl \rightarrow CH_4$ pathway (Table 1) describes the general reaction mechanism. However, no direct evidence could be furnished on this mechanism, because the decomposition is very fast, and halogen transfer reactions of H- and Cl-containing methanes are slow as compared to oxygen addition. The higher dissociation energy of C-H and C-Cl bonds of dichloromethane can explain the lower decomposition rate of CH_2Cl_2 as compared to $CHCl_3$

$CFCl_3$-O_2 System. In this case the electrons cleave the C-Cl bond, and the number of fluorine atoms bounded to the carbon atom increases due to halogen transfer reactions. The intermediates in this system are CF_2Cl_2, $COCl_2$, $COClF$ and COF_2. The final products, CF_3Cl, CF_4 CO_2, Cl_2 and F_2 are harmless to the environment. The phosgene type molecules are formed via the electron collision reactions. The next probable step is the addition of oxygen atom or oxygen molecule and hence, formation of peroxy- and/or oxy-radicals. The collision of halogenated methyl radical with halogenated methane produces halogen molecules, other more fluorinated methanes and less fluorinated radicals. According to the general reaction mechanism $CCl_4 \leftarrow \mathbf{CFCl_3} \leftrightarrow CF_2Cl_2 \leftrightarrow CF_3Cl \rightarrow CF_4$ formation of CCl_4 is expected (Table 1). However, due to its high decomposition rate and small quantity, CCl_4 could not be detected.

CF_2Cl_2-O_2 System. The widest product distribution, containing $CFCl_3$, CF_3Cl, CF_4, $COCl_2$, $COClF$, COF_2, CO_2, Cl_2 and F_2 was measured in this case. The special feature of particular system is that all chlorofluoromethanes were formed, contrary to other CFC-O_2 mixtures in which mainly more fluorinated methanes were detected as products. It is explained by the different decomposition rates of reactants on the one hand, and the different C-F and C-Cl bond energies on the other hand. According to the suggested reaction mechanism $CF_{A-1}Cl_{B+1}$, $CF_{A+1}Cl_{B-1}$, $CF_{A+2}Cl_{B-2}$, and $CF_{A+3}Cl_{B-3}$ can form as intermediates and products, respectively. All products of the $CFCl_3 \leftrightarrow \mathbf{CF_2Cl_2} \leftrightarrow CF_3Cl \rightarrow CF_4$ pathway were identified in this system.

CF_3Cl-O_2 System. Although the general mechanism suggests the $CF_2Cl_2 \leftrightarrow \mathbf{CF_3Cl} \rightarrow CF_4$ pathway, CF_2Cl_2 was not detected in the products. It is very probable that the C-F bond was not cleaved in CF_3Cl. The main reaction product was CF_4, which is harmless to the environment. Other products include Cl_2, F_2 and CO_2, which formed through peroxy- and oxy radicals.

During the decomposition of CFCs, the higher is the energy of C-F and C-Cl bonds, respectively, the slower is the decomposition rate (Figs. 1 and 2). In the presence of oxygen two decomposition pathways were found for the models studied in this work. The first mechanism involves $CF_{A-1}Cl_{B+1} \leftrightarrow CF_ACl_B \leftrightarrow CF_{A+1}Cl_{B-1} \leftrightarrow CF_{A+2}Cl_{B-2} \rightarrow CF_{A+3}Cl_{B-3}$ pathway (Table 1). It is well known that the higher is the fluorine content of CFC, it has the less ozone depleting potential. Thus, products of the above pathway, namely CF_3Cl and CF_4, are not harmful to the environment. The other pathway leads to the formation of CO_2, Cl_2 and F_2 through peroxy- and oxy radicals, and also carbonyl compounds. Thus, it can be concluded that methanes containing Cl, and/or F and/or H atoms can be transformed into harmless and/or valuable products in silent electric discharge [12].

Table 1. Boundary conditions for CCl_4, $CHCl_3$, CH_2Cl_2; F can substitute H; CH_CCl_D= model compound; $C+D=4$; $C_{max}= D_{max}=3$;

Electron collision reactions:

1. $CH_CCl_D + e \rightarrow CH_{C-1}Cl_D + H + e$
2. $CH_CCl_D + e \rightarrow CH_CCl_{D-1} + Cl + e$
3. $CH_{C-1}Cl_{D-1} + e \rightarrow CH_{C-2}Cl_{D-1} + H + e$
4. $CH_{C-1}Cl_{D-1} + e \rightarrow CH_{C-1}Cl_D + Cl + e$
5. $O_2 + e \rightarrow O + O + e$
6. $Cl_2 + e \rightarrow Cl + Cl + e$
7. $H_2 + e \rightarrow H + H + e$

Recombinations:

8. $CH_{C-1}Cl_D + Cl \rightarrow CH_{C-1}Cl_{D-1}$
9. $CH_{C-1}Cl_D + H \rightarrow CH_CCl_D$
10. $CH_CCl_{D-1} + Cl \rightarrow CH_CCl_D$
11. $CH_CCl_{D-1} + H \rightarrow CH_{C-1}Cl_{D-1}$
12. $Cl + Cl \rightarrow Cl_2$
13. $H + O \rightarrow OH$
14. $H + O_2 \rightarrow HO_2$
15. $H + Cl \rightarrow HCl$

Halogen transfer reactions:

18. $CH_CCl_D + CH_{C-1}Cl_D \rightarrow CH_{C-1}Cl_D + CH_CCl_D$
19. $CH_CCl_D + CH_{C-1}Cl_D \rightarrow CH_CCl_{D-1} + CH_{C-1}Cl_{D-1}$
20. $CH_CCl_D + CH_CCl_{D-1} \rightarrow CH_{C-1}Cl_D + CH_{C-1}Cl_{D-1}$
21. $CH_CCl_D + CH_CCl_{D-1} \rightarrow CH_CCl_{D-1} + CH_CCl_D$

Formation of peroxy radicals

22. $CH_{C-1}Cl_D + O_2 \rightarrow CH_{C-1}Cl_DO_2$
23. $CH_CCl_{D-1} + O_2 \rightarrow CH_CCl_{D-1}O_2$

Formation of haloalkoxy radicals:

25. $2\ CH_{C-1}Cl_DO_2 \rightarrow 2\ CH_{C-1}Cl_DO + O_2$
26. $2\ CH_CCl_{D-1}O_2 \rightarrow 2\ CH_CCl_{D-1}O + O_2$
27. $CH_{C-1}Cl_D + O \rightarrow CH_{C-1}Cl_DO$
28. $CH_CCl_{D-1} + O \rightarrow CH_CCl_{D-1}$

Revelation of carbonyl compounds:

30. $2\ CH_{C-1}Cl_DO \rightarrow 2\ CH_{C-2}Cl_DO + H_2$
31. $2\ CH_CCl_{D-1}O \rightarrow 2\ CH_{C-1}Cl_{D-1}O + H_2$

Self-degradation of carbonyl compounds and formation of carbon dioxide

32. $CH_{C-2}Cl_DO \rightarrow CH_{C-3}Cl_DO\ [COCl] + H$
33. $CH_{C-1}Cl_{D-1}O \rightarrow CH_{C-2}Cl_{D-1}O + H$
34. $CH_{C-2}Cl_DO + OH \rightarrow CH_{C-3}Cl_DO\ [COCl] + H_2O$
35. $CH_{C-1}Cl_{D-1}O + OH \rightarrow CH_{C-2}Cl_{D-1}O + H_2O$
36. $CH_{C-3}Cl_DO + OH \rightarrow CO + H_2O/HOCl$
37. $CH_{C-2}Cl_{D-1}O + OH \rightarrow CO + H_2O/HOCl$
38. $CH_{C-3}Cl_DO + O_2 \rightarrow COH_{C-3}Cl_DO_2$
39. $CH_{C-2}Cl_{D-1}O + O_2 \rightarrow COH_{C-2}Cl_{D-1}O_2$
40. $2\ COH_{C-3}Cl_DO_2 \rightarrow 2\ COH_{C-3}Cl_DO + O_2$
41. $2\ COH_{C-2}Cl_{D-1}O_2 \rightarrow 2\ COH_{C-2}Cl_{D-1}O + O_2$
42. $COH_{C-3}Cl_DO \rightarrow H/Cl + CO_2$
43. $COH_{C-2}Cl_{D-1}O \rightarrow H/Cl + CO_2$

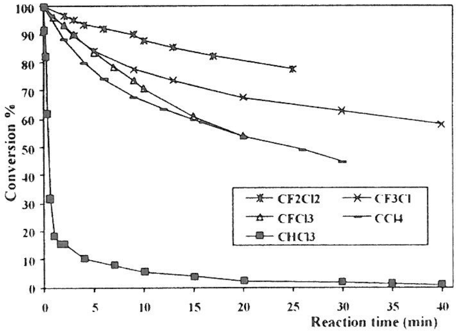

Fig. 1. Conversion of model compounds against the reaction time in the presence of argon

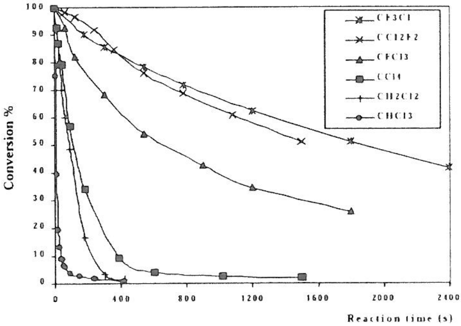

Fig. 2. Conversion of model compounds against the reaction time in the presence of oxygen

Acknowledgement

This work has been supported by the Hungarian Scientific Research Fund (Project No. T29734).

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