

Decomposition of Halogenated Methane Derivatives in Silent Electric Discharge

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2002

1. INTRODUCTION AND AIMS

People living in modern age have tended to conquer and exploit the nature. These processes led to the increasing employment and the overbalance of the nature. Nowadays one of the most important problems is the protection of environment from these harmful effects, and efficient environmental protection cannot be imagined without complete chemical knowledge. Environmental chemistry aims at revealing the chemical processes of the natural environment and removal of harmful compounds by means of chemical information and methods.

The atmosphere is a part of biosphere, hence its protection is as important as any other part of that. Pollutants could change the state and properties of the atmosphere, hence could cause climatic and meteorological changes endangered the vital conditions of the Earth.

There turns up more and more serious news about the ozone hole and global warming. Chlorofluorocarbons (CFCs, Freons) facilitate the development of these environmental damages caused by human beings. The use of these halogenated hydrocarbons - first of all as aerosols, cooling, refrigerating and carrying agents- started in the middle of the 60s and their widespread development occurred in the '70s last century. There were many causes of spread, these were low cost, non-flammable, inert and non-toxic compounds of high heat capacity and low boiling point. These materials were supposed to be ideal for practical applications. In spite of these facts it turned out in the last three decades that these compounds are harmful for the environment, contribute to global warming and to the reduction of the ozone concentration in the stratosphere. Hence, the use and production of some CFCs were restricted or banned by GEF (Global Environment Facility) and Montreal Protocol (in 1986).

The environmentally safe decomposition of stocked CFC reserves is of great theoretical and practical importance. The methods applied for the decomposition of CFCs before are expensive and do not fulfill the requirements of environmental protection and technology.

The aim of my work was to study the decomposition of different fluoro- and/or chloromethanes in silent electric discharge. CCl_4 , CFCl_3 , CF_2Cl_2 and CF_3Cl were chosen as model compounds containing chlorine and fluorine, in addition CHCl_3 and CH_2Cl_2 were investigated experimentally because of their chlorine and hydrogen content.

My work was also aimed at finding correlations between chemical nature of model compounds and their decomposition rate and identifying the product distributions as a function of reaction time.

It was an interesting aim of my work to clear up whether the kinetic reaction mechanism of the decomposition depends on the presence of oxygen or not.

Goal of mine was also to describe the chemical reaction mechanism of the decomposition furthermore to get information about the kinetic parameters of elementary steps and to perform thermochemical calculations in order to justify the conclusions applied for the mechanisms of the processes.

My work was aimed at providing information on processes of the decomposition of freons in the atmosphere, as well.

2. METHODS APPLIED FOR INVESTIGATIONS AND ANALYSIS

Three static reactors were used in the experiments simultaneously. They were closed systems filled up with gas mixtures of given pressure and concentration. The measurements were carried out at 11 kV and the temperature was kept constant at 298 K. The double glass walls of the cylindrical shaped reactor served as a dielectric layer. There was water in the inner cylinder and outside of the outer cylinder, working as an electrolyte solution connected the electrodes to the reactors. The reaction time was started by the turning on and ended by the turning off the mains. After the end of the experiment samples were taken from the reactor for analysis.

The purity level of all the model compounds (CCl_4 , CHCl_3 , CFCl_3 , CF_2Cl_2 and CF_3Cl) and the diluent argon and oxygen gases was 99.99%. All model compound (11.67 V/V%)-argon (88.33 V/V%) mixtures were decomposed at pressures of 200, 300, 400 torr.

Decomposition products of CCl_4 -Ar and CHCl_3 -Ar systems were separated by solvent extraction. A 0.1 M sodium-hydroxide solution (10 cm^3) and dichloromethane (2 cm^3) were injected into the reactors simultaneously. The CH_2Cl_2 contained 0.1 V/V% toluene as an internal standard to avoid errors of measurements due to the fast evaporation of CH_2Cl_2 . After the products having been dissolved, inorganic and organic phases were separated and analyzed. The organic products solved in CH_2Cl_2 were analyzed by gas chromatography. Inorganic products were measured by UV-VIS spectrophotometry.

The gaseous products of CFCl_3 -Ar, CF_2Cl_2 -Ar, CF_3Cl -Ar and all the oxygen-diluted mixtures were analyzed by UV spectrophotometry and by FT-IR spectroscopy, respectively. The gas mixture containing the products was expanded from the reactor into an evacuated cylindrical UV cell. After the UV measurement the gas mixture was introduced into an FT-IR cell and analyzed by FT-IR spectroscopy.

3. NEW SCIENTIFIC RESULTS

3.1. Decomposition of halomethanes in the absence of oxygen

According to the results of the reaction kinetic experiments it was concluded that all the model compounds could be decomposed in silent electric discharge, though their decomposition rates were different.

The slowest rate could be measured in the freon-argon systems, these were followed by the decomposition rate of carbon tetrachloride and the hydrogen containing methanes were decomposed by the fastest rate.

The spectra of products strongly depended on the composition of model compound. The main route of the CFC decomposition could be assumed by the halogentransfer reaction, as follows:



According to the chemical evidences and information originating from the literature, the initial step of the decomposition of all systems is the



electron-collision reaction, which is followed by the halogentransfer and recombination reactions.

The halogentransfer reaction of carbontetrachloride leads to re-formation of the model compound, whereas these reactions of the chlorine and fluorine containing methanes as model compounds results the other CFCs as products.

The decomposition of chloroform is very fast compared to that of the other systems and yields a wide product spectrum. The H and Cl abstraction taken place on the chloroform facilitate the fast chain decomposition of the model compounds. This process leads to the recombination reactions via formation of radicals, accompanying with the production of chlorinated ethanes, ethenes of high amount. The elimination reaction of ethanes gives further ethyl radicals, hence leading to the formation of propanes in recombination reactions.

Results of decomposition of halomethanes occurring in the absence of oxygen can be assumed as follows:

The initial step of the process is the electron-collision reaction of model compounds leading to the formation of radicals in silent electric discharge:

- The decomposition of carbontetrachloride can be explained by the recombination of radicals.
- The dominant processes of the chlorofluoromethane decomposition are the halogentransfer reactions taking place by short chaincycles.
- Hydrogen containing compounds decompose in long chaincycles giving wide spectrum of products.

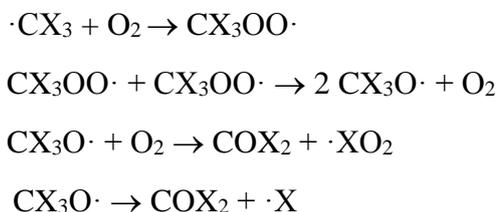
3.2. Decomposition of halomethanes in the presence of oxygen

The decomposition of halogenated methanes speeded up in the presence of oxygen, accompanying with the complete discontinuance of ozone formation. Furthermore the decomposed gas mixtures have almost completely different product spectra compared to that of the argon diluted gas mixtures.

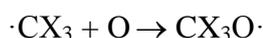
The decomposition of oxygen molecules and model compounds by electron-collision reaction, being the initial steps of the process, leads to the formation of O, H, Cl, F and haloalkyl radicals.

The H-elimination reaction of hydrohalomethanes results in hydroxyl radicals, which also can react with other molecules and radicals.

The haloalkyl radicals can add oxygen-molecules leading to the formation of peroxy-radicals.

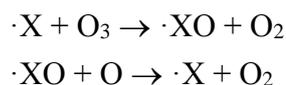


The main intermediers of the decompositions are carbonyl-halogenid products, which can be formed in the following reaction:



The decomposition rate of fluorine containing products changes only by three times faster in the presence of oxygen. It means that the reactions written above are not of great practical importance, as it is proved by thermochemical calculations as well.

The prevention of ozone formation by model compounds can be explained by their oxygen-atom-impact reactions. My results can also prove that the following reaction-cycle,



being well-known from the ozone chemistry, accounts for the depletion of ozone in our systems and in the stratosphere as well.

The model compound decomposition in the presence of oxygen could be assumed in the statements as follows:

- The decomposition rate of model compound increased in the presence of oxygen. This could be explained by the formation of reactive oxygen radicals and their H elimination reaction.
- The decomposition of chlorofluoromethanes speeded up in the presence of oxygen as well.
- The haloalkyl radicals, formed in electron collision reaction could add oxygen molecule for atom accompanying with the formation of oxo and peroxy radicals, respectively.

3.3. Kinetic modeling and thermochemical calculations

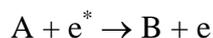
For the mathematical modeling of kinetic mechanisms it is important to know the kinetic parameters of the electron collision reaction. The number of successful electron-molecule collision reaction (Z_D) can be calculated by the following equation, if it is supposed that the initial reaction step is the bond scission caused by the colliding electrons:

$$Z_D = Ze^{-\frac{D}{E\lambda}}$$

where Z is the number of all collisions, D is the activation energy of the particular reaction (in our case it is the bond scission energy) and $E\lambda$ the mean energy of the electrons (E and λ are the accelerating voltage of the electric field and mean free path of the electrons, respectively).

According to my calculations the mean kinetic energy of electrons equals 0.65 eV in the presence of argon.

The rate of a general equation



can be calculated by the following way.

$$r = \frac{d[B]}{dt} = k[A] = \frac{Qd}{V_r} k^* [A]$$

where V_r means the reactor volume, Q is the charge, d is the mean free path of the electrons and k^* is a normalized rate coefficient being independent of the reactor parameters.

It is supposed that the rate coefficient of the particular reaction step is related to the number of successful collision (Z_D). In this way the rate coefficient of a particular reaction can be calculated by the ratio of two rate coefficients, as follows:

$$\frac{k_A}{k_B} = \frac{Z_{D,A}}{Z_{D,B}} = e^{-\frac{D_A - D_B}{E\lambda}}$$

The calculated rate coefficients can be found in the following table.

The calculated rate coefficients of the electron-collision reactions

No.	Reactions	D / kJmol ⁻¹	K _{No.} /k ₁	k / s ⁻¹
1	CCl ₄ + e* → ·Cl + ·CCl ₃ + e	288	1	4,15 · 10 ⁻⁴
2	CF ₃ Cl + e* → ·F + ·CF ₂ Cl + e	490	0,030	1,26 · 10 ⁻⁵
3	CF ₃ Cl + e* → ·Cl + ·CF ₃ + e	360	0,079	3,28 · 10 ⁻⁵
4	CF ₂ Cl ₂ + e* → ·F + ·CFCl ₂ + e	462	0,031	1,29 · 10 ⁻⁵
5	CF ₂ Cl ₂ + e* → ·Cl + ·CF ₂ Cl + e	346	0,199	8,27 · 10 ⁻⁵
6	CFCl ₃ + e* → ·F + ·CCl ₃ + e	435	0,024	1,01 · 10 ⁻⁵
7	CFCl ₃ + e* → ·Cl + ·CFCl ₂ + e	305	0,569	2,36 · 10 ⁻⁵
8	CHCl ₃ + e* → ·H + ·CCl ₃ + e	322	0,192	7,96 · 10 ⁻⁵
9	CHCl ₃ + e* → ·Cl + ·CHCl ₂ + e	393	0,143	5,94 · 10 ⁻⁵
10	CH ₂ Cl ₂ + e* → ·H + ·CHCl ₂ + e	339	0,222	9,20 · 10 ⁻⁵
11	CH ₂ Cl ₂ + e* → ·Cl + ·CH ₂ Cl + e	412	0,070	2,91 · 10 ⁻⁵

The modeling of the electron-collision reaction and the kinetic mechanism was performed by a computer code ZITA by means of the radical- and atom-recombination reaction rate data found in the literature. The results of the simulations were the evaluation of the rate of the elementary steps could not be found in the literature yet.

The model fulfills the requirements on the description of decomposition of fullhalogenated methanes in argon atmosphere. The models for other systems were incomplete because of the wide product spectra and of the high number of the missing rate coefficients.

A complete model on the decomposition of H containing halomethanes could be proposed only after the detailed investigation of their product distribution.

Thermochemical calculations were presented for justifying the experimental results. It was supposed that the main process, after the atomization, is to tend to the formation of compounds being in the state of energy-minimum. Although the calculated product distribution differs in the calculated and in the investigated systems, but the theoretical results supported the experimental product spectra.

The results of model compound decomposition in the presence of oxygen could be assumed in the statements as follows:

- A general reaction mechanism was suggested to all the investigated systems.
- The reaction coefficients of the electron collision reactions were calculated by means of the thermochemical data and laws of discharge taken place in gas phase.
- The unknown rate coefficients of halogentransfer reaction were determined.
- Thermochemical calculations were performed in order to verify the experimental results.

My work contributed the augmentation of information on atmospheric chemistry and reaction kinetics of freons in the absence and presence of oxygen. Although there are problems having to solve yet, for example the scrubbing of the outgoing gas phase, the silent electric discharge is a suitable tool for the decomposition of halogenated methanes.

4. PUBLICATIONS:

4.1. Publications relevant to the thesis

4.1.1. Papers

1. **K.A. Főglein**, J. Szépvölgyi, A. Dombi:
Decomposition of halogenated methanes in oxygen-free gas mixtures by the use of a silent electric discharge; **Chemosphere**, 46, (2002) (in press)
2. **K.A. Főglein**, A. Dombi:
Decomposition of halogenated methanes in oxygen containing gas mixtures by the use of a silent electric discharge; **Chemosphere**, (accepted for publication)
3. **K.A. Főglein**, A. Dombi:
Reaction kinetic modeling of halogenated methanes in silent electric discharge **Reaction Kinet. Catal Lett**, (submitted for publication)

4.1.2. Complete Proceedings

1. **Katalin Főglein**, András Dombi:
Decomposition of Halogenated Hydrocarbons in Silent Electric Discharge
2nd Int. Conf. On Environmental Engineering, 1999. május 29,- június 2., Veszprém
2. **Katalin Főglein**, András Dombi
Decomposition of CFCs in silent electric discharge
Workshop on VOC Analysis and Degradation, 1999 december 15-16, Gent

4.1.3. Presentations

1. **Főglein Katalin**, Tóth Adrienn, Dombi András
Halogéntartalmú szénhidrogének átalakítása csendes elektromos kisülésben
XX. Kémiai Előadói Napok, 1997. október 13-15., Szeged
2. **Főglein Katalin**, Dombi András
Halogéntartalmú szénhidrogének vizsgálata csendes elektromos kisülésben
XXI. Kémiai Előadói Napok, 1998. október 13-15., Szeged
3. **Katalin Főglein**, Adrienn Tóth, András Dombi
Decomposition of Halogenated Hydrocarbons in Silent Electric Discharge
3. Nemzetközi Környezetvédelmi Szakmai Diákkonferencia, 1998. június 24-26., Mezőtúr
4. **Katalin Főglein**, András Dombi
Decomposition of Halogenated Hydrocarbons in Silent Electric Discharge
3rd International Symposium Interdisciplinary Research, 1998. szeptember 24-25., Újvidék
5. **Főglein Katalin**, Dombi András, Szépvölgyi János
Halogéntartalmú szénhidrogének átalakulásának vizsgálata csendes elektromos kisülésben
XXII. Kémiai Előadói Napok, 1999. október 13-15., Szeged

4.1.4. Posters:

1. **Főglein Katalin**, Tóth Adrienn, Dombi András
Decomposition of Halogenated Hydrocarbons in Silent Electric Discharge
Inorganic Reaction Mechanism Meeting 97, 1998 január 8-10, Debrecen

4.2. Publications not relevant to the thesis

1. I. Ilisz, **K. Főglein**, A. Dombi
The photochemical behavior of hydrogen peroxide in near UV-irradiated aqueous TiO₂ suspensions; **Mol. Catal. A. Chem.**, 135 (1998) 55.
2. **Katalin A. Főglein**, Pál T. Szabó, Irina Babievskaya and János Szépvölgyi
Comparative Study of Decomposition of Carbon tetrachloride in Thermal Plasma
Plasma Chemistry and Plasma Processing (submitted for publication)
3. **Katalin A. Főglein**, Pál T. Szabó, Irina Babievskaya and János Szépvölgyi
Comparative Study of Decomposition of Chloroform in Thermal Plasma
Plasma Chemistry and Plasma Processing (submitted for publication)
4. **Katalin A. Főglein**, Irina Babievskaya and János Szépvölgyi
Thermodynamic Calculations for n-Hexane and Toluene Decomposition in RF Thermal Plasma
Plasma Chemistry and Plasma Processing (submitted for publication)
5. **K. A. Főglein**, J. Szépvölgyi
Decomposition of Hazardous Organic Compounds in RF Thermal Plasma
International Symposium on Plasma Chemistry, Gremi/CNRS, 2001. július 9-14., Orleans