DECOMPOSITION OF 1,2-DICHLOROETHANE IN HYDROGEN BY NON-EQUILIBRIUM RF PLASMA

G.Schulz[1], G.Birkhahn[2], I.Börger[2], J.Lachmann[2]

Universität Potsdam
Institut für Physikalische und Theoretische Chemie
Arbeitsgruppen Plasmachemie[1] u. Plasmapyrolyse[2]
Rudower Chausse 5, Geb. 1.5, 12484 Berlin, Germany

The non-thermal destruction process of 1,2-dichloroethane (DCA) has been experimentally investigated using a capacitively coupled rf hydrogen plasma (CCP) which operates at medium pressure (20 hPa) and low power (10-300 W). The destruction efficiency for DCA is >99%. More than 80 mol% of the parent carbon from DCA is converted into C_1-C_2 hydrocarbon species. A reaction model of the overall decomposition process basing on a GC/MS-measured product distribution is suggested.

INTRODUCTION

Numerous papers on the subject of "Plasma contra CFC´s" recently been published point to an increasing interest in such processes [1]. Regarding to conventional incineration approaches, plasma technologies offer alternative methods to remove halogenated hydrocarbon wastes. For instance, the disposal of hazardous halocarbons under reducing plasma conditions prevents the formation of undesirable by-products of the incineration such as dioxin. Moreover, a non-equilibrium plasma particularly is an attractive generator of reactive free radicals and species in highly excited states already at low gas temperatures. In this study, the destruction of 1,2-dichloroethane in a non-thermal hydrogen plasma are described. The results are compared with those obtained in a thermal Ar/H_2 plasma jet [2].

EXPERIMENTAL

The experiments has been carried out in a capacitively coupled rf plasma (CCP) at a pressure of 20 mbar (Fig. 1). The 1 kW rf generator (Steremat Berlin) operates at a frequency of approximately 4 MHz. The air cooled reactor manufactured from quartz glass is 20 mm in diameter and 300 mm in length. Two copper ring electrodes transferring the power (10-320 W) from the rf generator to the plasma are attached outside of the tube

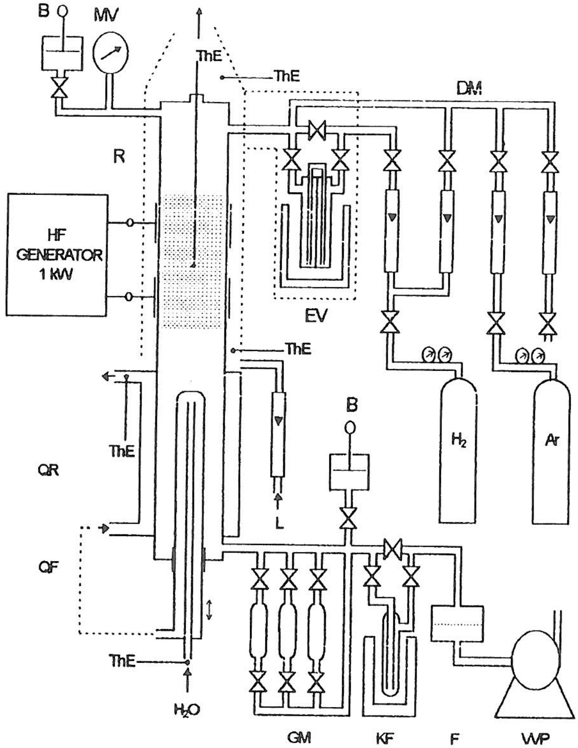

Fig. 1: Scheme of reactor device

ensuring very pure reaction conditions. The feed mixture consisting of the plasma carrier gas hydrogen (1.5 mol/h) and the vaporized 1,2- dichloroethane (0.065 mol/h) (EV) is injected tangentially through an inlet above the plasma. The temperature of the neutral gas is measured with a quartz-shielded thermocouple (ThE) inserted axially into the centre of the plasma column. The power picked up from the plasma was estimated calorimetrically by an air-cooled device which surrounds the reactor as a jacket. The gaseous reaction products filled into sample tubes (GM) were analyzed gaschromatographically by a GC/MS system ITD 800 and by a gaschromatograph 3600 (FINNIGAN).

With the given pressure (20 mbar) and in the present power range (10-320 W), the plasma column fills in the whole cross-section of the discharge tube and is extended between the electrodes; the plasma volume is $V_{pl} = 30\ cm^3$.

According to calorimetric measurements of the heat balance of the cooling air flowing through the calorimetric jacket, the power transmitted to the plasma can be estimated from

$$N_l = 0.63 * N_{el}$$

($N_{el} = U_a * \Delta i_a$, U_a anode voltage, Δi_a difference between the anode current under load and the anode current without load, see Fig. 2).

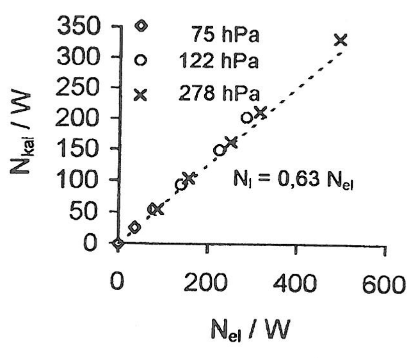

Fig. 2: Calorimetrically measured power vs. electric generator power Ua*ΔIa, for various pressures in an Ar plasma

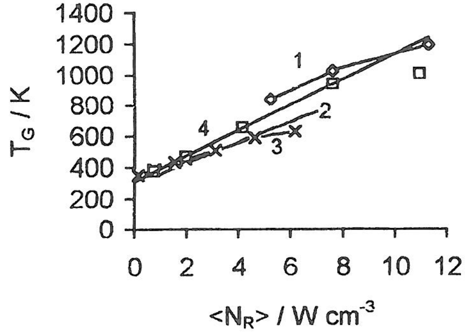

Fig. 3: Gas temperature vs. power density
1 [5] CCP 35 MHz H_2 27 mbar
2 [8] CCP 13 MHz CO_2 2-13 mbar
3 own CCP 4 MHz Ar 20 mbar
4 own CCP 4 MHz H_2 20 mbar

The gas temperature within the discharge measured with a thermocouple which is fully surrounded by the plasma increases proportional to the power density. This dependence is given by the equation:

$$T_G/K = 85,1 \langle N_R \rangle + 300$$

($\langle N_R \rangle$/W cm^{-3} , power density = measured power / plasma volume V_{pl}). Differences from the straight line at $\langle N_R \rangle = 11$ W/cm^3 is explained by an increasing radiative losses from the probe. Fig. 3 shows the measured gas temperature as a function of power density in comparison with results obtained for other rf plasmas (CCP's).

Table 1: Experimental conditions:

sample	D_{H2} mol/h	m_{DCA} mol/h	p_R mbar	N_R W	$\langle N_R \rangle$ W/cm^3	t_V s	$\langle E \rangle$ J/cm^3	T_G K
1	1.5	0.068	20	10	0.33	0.097	0.032	330
2	1.5	0.062	20	50	1.67	0.073	0.122	440
3	1.5	0.065	20	138	4.60	0.046	0.212	690
4	1.5	0.061	20	320	10.67	0.027	0.288	(1200)

t_V = residence time, $\langle E \rangle$ = energy density = $\langle N_R \rangle * t_V$

RESULTS AND DISCUSSION

The reaction products were grouped and were plotted as mol fraction carbon (mol % carbon) relative to the parent carbon versus energy density $\langle E \rangle$ (see Fig. 4).

The concentration of DCA diminishes exponentially and, at $\langle E \rangle > 0.212$ J/cm^3, the conversion of DCA is >99 %. The group of the chlorinated hydrocarbon products (CHC) consists of CH_3Cl, CH_2Cl_2, C_2H_3Cl, C_3H_5Cl, $C_2H_2Cl_2$, and $C_3H_6Cl_2$,. Particularly at the lowest energy density of 0.032 J/cm^3, chloroethene dominates in this group sharing by more than 85%, and, like the other chlorinated species, chloroethene has here its concentration maximum. Only chloromethane achieves its maximum concentration of 0.4 mol% carbon just at 0.122 J/cm^3. More than 80 mol% of the parent carbon is converted into the hydrocarbon species C_2H_2, CH_4, and C_2H_4, which form the C_1-C_2 HC group. The major product is C_2H_2 with a maximum concentration of about 53 mol% carbon followed by CH_4 with 27 mol% carbon. With the sequence of C_2H_4, CH_4, C_2H_2,

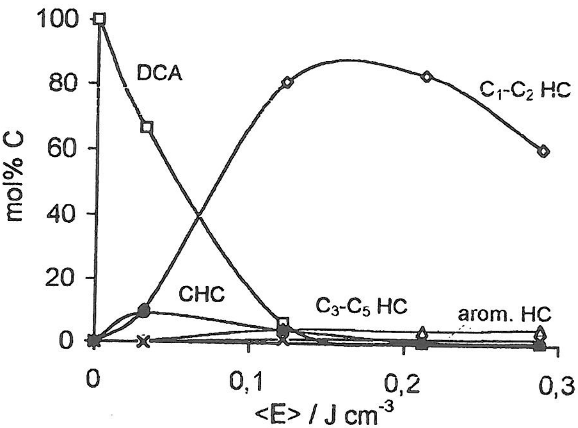

Fig. 4: Measured concentration profiles of product groups of the DCA decay vs. energy density

the marked maxima of these hydrocarbons shift to higher energy densities.

The C_3-C_5 HC group and the group of the aromatic hydrocarbons contain species like C_3H_4, C_4H_2, C_4H_4, C_5H_6 as well as C_6H_6 and C_6H_5-CH_3, respectively. With increasing energy density, all of them show a slow increase of their concentrations without formation of a maximum, finally turned into a nearly constant region at the higher energy densities. The soot concentration (no curve) determined by carbon balance increases with increasing energy density and achieves 27 mol% C at $<E> = 0.288$ J cm^{-3}. Apart from the measured CKW products above mentioned, only HCl was identified as a Cl species in all gas samples by neutralization with NaOH; Cl_2 was not detectable by GC/MS analyses under these experimental conditions [3].

The fast overall decomposition of the DCA characterized e.g. for sample 3 ($<E> = 0.212$ J cm^{-3}, $t_V = 0.046$ s, $T_G = 690$ K) by a high rate constant of $k = 120$ s^{-1} is not explainable by thermal processes. With the measured gas temperatures, the corresponding k - values for the thermal decomposition of the DCA are 10^3 - 10^4 times lower [4]. Supported by investigations in [5] carried out under similar plasma conditions, it is supposed that non-equilibrium plasma processes cause the decomposition of the DCA at the given pressure range. Initiated by primary reactions

$$H_2 + e^- \longrightarrow H + H + e^-$$ and

$$C_2H_4Cl_2 + e^- \longrightarrow C_xH_yCl_z + R + e^- \qquad (R = H, Cl, CH_2Cl),$$

the decomposition process within the starting phase are continued by following reactions of the free-radicals R with the parent molecule

$$C_2H_4Cl_2 + R \longrightarrow P \qquad (P = C_iH_jCl_k, Cl, H, HCl).$$

The activation energies of these reactions are partially lower than 30 kJ/mol explaining the observed fast DCA destruction. As kinetic calculations indicated [2,6], such initial radical processes are not relevant for the DCA conversion under the thermal conditions of a 25 kW Ar/H_2 plasma jet. Fig. 5 shows a comparison of both product spectra measured in the CCP as well as in the plasma jet [2] (see also Table 2). Apart from a lower DCA conversion, the product distribution of the CCP experiment indicates a substantially higher methane concentration as well as the appearance of chloro- and dichloro-

Table 2: Experimental conditions for the DCA destruction in the non-equilibrium rf plasma (CCP) and in the thermal plasma jet (PJ)

parameter		rf plasma (CCP)	plasma jet (PJ)
power	kW	0.138	20
gas temperature	K	690	3500
pressure	bar	0.02	1
H_2 gas flow	mol/h	1.5	127
DCA flow rate	mol/h	0.06	13
residence	ms	46	0.1
DCA conversion	%	>99,5	>99.9

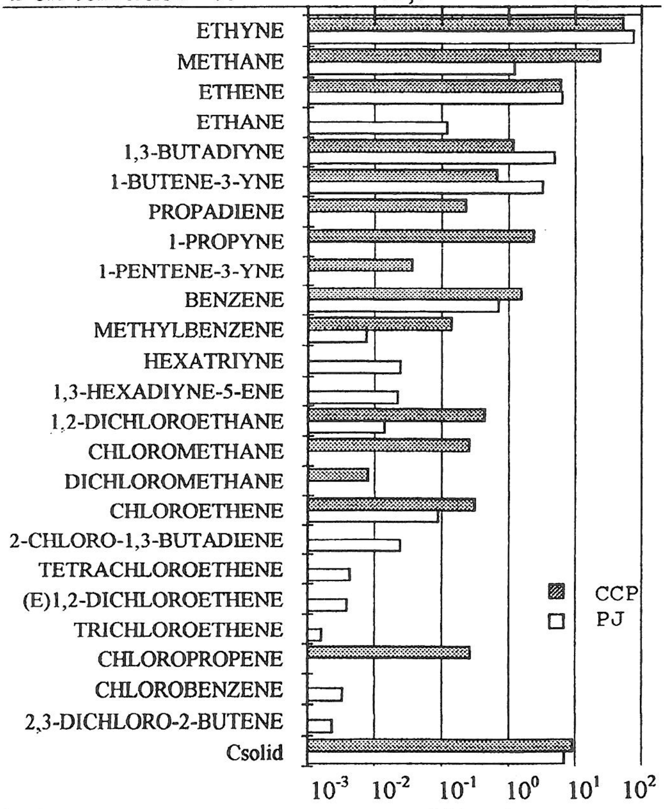

Fig.5:

Product profiles of the 1,2-dichloroethane conversion for the non-equilibrium rf plasma (CCP) and for the thermal plasma jet (PJ) (exp. conditions see Table 2)

methane and C_3 -hydrocarbon compounds (HC). HC and CHC aliphatics with more than 5 carbon atoms or 2 chlorine atoms, respectively, were not observed. Probably, this is leaded to the fact, that under the non-thermal plasma conditions of the CCP other reaction paths are treaded in comparison with the plasma jet process.

This detailed spectrum of the products and the observed succession of the product maxima allow to form a picture of the overall processes which take place with the DCA decomposition in the CCP (Fig. 6). By detachment of HCl, the first step of the DCA destruction is its conversion into secondary CHC´s, specially into CH_2Cl_2 and C_2H_3Cl. In the following, these CHC´s either converts further to C_1/C_2 HC´s by release of HCl or form higher molecular CHC´s (e.g. C_3H_5Cl) which are also convert into analogous HC´s. Furthermore, the hydrocarbons decompose by successive separation of H_2 from C_1/C_2 species over C_3/C_6 products to soot as described in the literature [7].

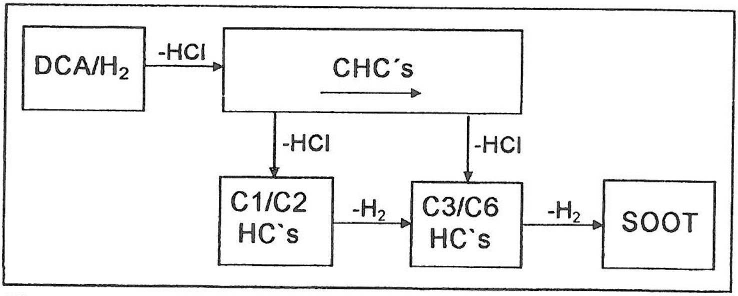

Fig. 6: Reaction scheme of the overall decomposition of 1,2-(DCA) in the capacitively coupled hydrogen rf plasma (CCP)

CONCLUSION

Generalizing the results, one can say, that the capacitively coupled non-equilibrium rf plasma (CCP) operated at medium pressures and low gas temperatures is suitable for investigations of the decomposition of gaseous or vaporous halogenated hydrocarbons. The destruction of the hazardous waste molecules is dominated by energy efficient non-thermal activation processes and by reactive free radical species. With the impossibility of dioxin formation, decay of halocarbons in a hydrogen plasma lead mainly to C_1-C_2 hydrocarbons.

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