Kinetical Modeling of Chemical Processes During Conversion of Chlorinated Hydrocarbons in a Thermal Plasma

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Abstract
In this paper a kinetical modeling using a variation principle under irreversible thermodynamic conditions were applied to explain reaction structures of the conversion of chlorinated hydrocarbons, especially of 1,2-dichloroethane, in a hydrogen-argon plasma. The obtained results were compared with the experiment and with the result of a kinetical modeling assuming a special elementary reaction mechanism. The applications and conditions of this modeling method were discussed.

Introduction

Chlorinated hydrocarbons often are main constituents of industrial wastes. To clarify the formation of stable products as C_2H_2, CH_4, C_2H_4, C_2H_6, and HCl by thermal plasma decomposition experiments to the conversion of model substances (1,2-dichloroethane, trichloroethene) in the plasma jet of a 3,5 kW and a 20 kW plasmatron were realized at atmospheric pressure [1]. From these experiments time depended product distributions were determined in a wide range of temperatures (3800 K...2000 K) and of initial concentrations. After quenching, the identification and quantification of the reaction products were accomplished by gas chromatography-mass spectrometer (GCMS). The measurements were made at contact times of 10^{-4} s ...6.10^{-4} s.

The presence of chlorine in hydrocarbon systems causes a number of complications for the understanding of the kinetic factors during the decomposition. On account of the great variety of radical species occuring in high temperature C/H/Cl systems and the large number of rapid reactions between radicals, H, and Cl atoms the definition of a detailed kinetic mechanism is usually not possible. Informations about the intermediates, their secundary reactions and the values of the rate constants are often absent. However an approximate kinetical simulation may be helpful for the prediction of the behaviour of chlorinated hydrocarbons in complex mixtures of industrial wastes.

Modeling of 1,2-dichloroethane by a detailed mechanism and sensitivity analysis

A system of chemical reactions correspond to a set of differential equations for the concentrations c_i of the involved species :

$$\frac{d\vec{c}}{dt} = f\left(\vec{c}, \vec{k}\right); \quad \vec{c}(0) = \vec{c}_0 \qquad (1)$$

$\vec{c}(t)$ is the vector of the concentrations of the species and $\vec{k}$ is the vector of rate coefficients, describing the system .

In former investigations we found that stable hydrocarbons and HCl were optimally formed at T=2000 K ... 2200 K and t = 10^{-4}...$5 \cdot 10^{-4}$ s [1].

In order to investigate the significance of radicalic intermediates for the formation of the important products HCl, C_2H_2, C_2H_4, C_2H_6 and CH_4 in the temperature interval 2000 K ... 2200 K a sensitivity analysis was made by the program package KINAL [2]. This program used the sensitivity equations given by the differentiation of the chemical differential equations

$$\frac{\partial}{\partial \vec{k}}\left(\frac{\partial \vec{c}}{\partial t}\right) = \frac{\partial \vec{f}}{\partial \vec{c}}\frac{\partial \vec{c}}{\partial \vec{k}} + \frac{\partial \vec{f}}{\partial \vec{k}} \quad ; \quad \dot{\mathbb{S}}\left(t_2,t_1\right) = \mathbb{J}\left(t_2\right)\mathbb{S}\left(t_2,t_1\right) + \mathbb{F}\left(t_2\right) \qquad (2)$$

$\mathbb{S}$ is the local sensitivity matrix, $\mathbb{J}$ is the Jacobian of the function f (c, k) and $\mathbb{F}$ is the rate sensitivity matrix.

The redundant species regarding the important products were identified with KINAL by the method of the reduced models [3]. The species CH, CCl and Cl_2 were redundant at these temperatures. The importance of a reaction was determinated by the investigation of the rate sensitivity matrix $\mathbb{F}$, with

$$F_{ij} = \frac{k_j}{F_i(t_2)}\frac{\partial f(t_2)}{\partial k_j} = \frac{\nu_{ij} R_j\left(\vec{k}, \vec{c}\right)}{\sum_j \nu_{ij} R_j\left(\vec{k}, \vec{c}\right)} = \frac{\nu_{ij} R_j}{f_i} \qquad (3)$$

ν_{ij} is the stochiometric matrix, f_i is the rate of production of species i, and R_j is the rate of reaction j. KINAL carried out the principal component analysis of the matrix $\mathbb{F}$ and gave finally a recomendation for a reduced mechanism.

It was possible to reduce the mechanism from 85 reactions and 40 species to 39 reactions and 24 species without a significant change of the important product concentrations (Tab. 1).

Tab. 1: Reduced mechanism for the conversion of 1,2-dichloroethane in the plasma (2000 K-2200 K), $k = AT^B \exp(-E_a/RT)$

Nr.	reaction	lgA	B	E_a [kcal/mol]
1.	$C_2H_4Cl_2 = C_2H_4Cl + Cl$	16.0	.0	81.5
2	$C_2H_4Cl_2 = CH_2Cl + CH_2Cl$	17.2	.0	87.3
3	$C_2H_4Cl_2 = C_2H_3Cl + HCl$	13.6	.0	58.0
4	$C_2H_3Cl = C_2H_2 + HCl$	14.0	.0	69.3
5.	$C_2H_3Cl = C_2H_3 + Cl$	15.6	.0	91.7
6.	$C_2H_4Cl = CH_2Cl + CH_2$	17.2	.0	87.3
7.	$CH_2Cl + CH_2Cl = C_2H_4Cl_2$	13.0	.0	.0
8.	$CH_2Cl + HCl = CH_3Cl + Cl$	11.2	.0	.0
9.	$CH_3Cl = CH_3 + Cl$	15.4	.0	83.4
10.	$CH_3Cl + Cl = CH_2Cl + HCl$	13.3	.0	2.5
11.	$CH_2Cl + CH_3 = C_2H_5Cl$	13.7	.0	.0
12.	$C_2H_5Cl + Ar = C_2H_4 + HCl + Ar$	13.5	.0	36.6
13.	$CH_2Cl + H = CH_2 + HCl$	14.9	.0	15.1
14.	$HCl + H = H_2 + Cl$	12.7	.0	3.2
15.	$CH_3 + CH_3 = C_2H_6$	13.4	.0	.0
16.	$C_2H_5 = C_2H_4 + H$	13.3	.0	39.1
17.	$CH_3 + H_2 = CH_4 + H$	12.5	.0	10.2
18	$CH_3 + C_2H_3 = CH_4 + C_2H_2$	15.0	.0	.0
19.	$CH_2 + CH_2 = C_2H_4$	13.7	.0	.0
20.	$CH_2 + CH_2 = C_2H_2 + H_2$	14.1	.0.	.4

21.	$C_2H_3 + C_2H_3 = C_2H_4 + C_2H_2$	12.5	.0	.0
22.	$C_2H_3 + H = C_2H_2 + H_2$	13.3	.0.	.0
23.	$C_2H_3 + Ar = C_2H_2 + H + Ar$	14.9	.0	31.5
24.	$CH_3 + CH_3 = C_2H_4 + H_2$	16.0	.0	32.9
25.	$C_2H + H_2 = C_2H_2 + H$	13.2	.0	13.0
26.	$C_2H_6 + H = C_2H_5 + H_2$	9.2	1.5	3.7
27.	$C_2H_6 + Cl = C_2H_5 + HCl$	14.0	.0	1.0
28.	$C_2H_2 + Cl = C_2H + HCl$	14.2	.0	16.9
29.	$C_2H_4 + Cl = C_2H_3 + HCl$	14.0	.0	7.0
30.	$CH_4 + Cl = CH_3 + HCl$	11.9	2.0	1.5
31.	$CH_4 + H = CH_3 + H_2$	14.1	.0	11.9
32.	$CH_4 = CH_3 + H$	15.1	.0	104.0
33.	$C_2H_4 + Ar = C_2H_2 + H_2 + Ar$	17.4	.0	79.3
34.	$C_2H_4 + H = C_2H_3 + H_2$	7.2	2.0	6.0
35.	$C_2H_2 + H = C_2H_3$	13.6	.0	1.3
36.	$C_2H_2 + H = C_2H + H_2$	14.3	.0	19.0
37.	$C_2H + C_2H_2 = C_4H_2 + H$	13.5	.0	.0
38.	$C_4H_2 + C_2H = C_6H_2 + H$	13.6	.0	.0
39.	$C_2H_2 + Ar = 2C + H_2 + Ar$	13.6	.0	54.0

The application of a variation principle for the approximate calculation of the component distribution (irreversible thermodynamics)

In order to determine the distribution of chemical species of homogenous and closed chemically reacting systems by means of the thermodynamic basic equations a mathematical model was used under following conditions:

- The time gradient of the chemical potential was only determined by the thermodynamical functions of the system components .
- The transition to the thermodynamic equilibrium was considered as a transition of a certain physical system to the minimum of the potential energy Π of the system.
- The dynamics of the chemically reacting system under the influence of the energy Π determinated a trajectory of minimum energy dissipation.

The decrease of Π is equal to the increase of the uncompensated amount of heat Q^i

$$-\delta\Pi = \delta Q^i \qquad (4)$$

For a irreversible process Q^i is defined as

$$Q^i = T S^i = \int_0^t T\sigma\, d\zeta \qquad (5)$$

where T is the system temperature and σ is the entropy production due to the chemical reactions.

The potential energy Π of a gas-phase system is given by

$$\Pi = \sum_{i=1}^{k} \mu_i c_i$$

where c_i is the concentration of the component i and μ_i its chemical potential.

The equations of the material balance can be written as

$$\varphi_j = \sum_{i=1}^{k} c_i \nu_{ij} - b_j \qquad j = 1...m \qquad (6)$$

k - number of components in the homogenous system, ν_{ij} -stoichiometric coefficients, b_j - amount of the j^{th} element, m - number of elements in the system.

Using Eq. (6) the problem of the parameter estimation can be converted into a variation problem of minimizing of a function F (Π)

In connection with the Lagrangean polynomical approximation the mathematical function for this optimization problem is

$$F = \int_0^{\infty} \left\{ Q^i - \Pi + \lambda\varphi \right\} dt \rightarrow \min \qquad (7)$$

(λ - Lagrange parameter, t - time)
The linear Onsager theory gives for the entropy production σ near the equilibrium a quadratic dependence of the $\dot{c}_i$ [4] :

$$\sigma = \sum_{i=1}^{k} L_i \dot{c}_i^2 \qquad (8)$$

L_i is the diagonal matrix of the chemical phenomenological coefficients depending on the kinetics of the process. Usually the L_i are unknown.It is $L_i = L$ if catalytic and steric effects are neglegted and if all interactions of species are equal. Eq. (7) and (8) lead therefore to a set of linear expressions for the reaction rates as linear funktions of

$$A_i = \mu_i T^{-1} + \sum_{i=1}^{m} \nu_{ij} \lambda_j$$

the reaction affinities A_i. In this connection A_i.is the affinity of the reaction i in the ideal gas system.
This linear approximation is only justified for systems near the equilibrium. In fact the reaction rates are certain exponential expressions of the affinities, as the Arrhenius equation e.g..
Therefore the dissipation function σ were assumed to be in the following nonlinear approximation [5]

$$\sigma = L \sum_{i=1}^{k} \left(\dot{c}_i L^{-1} + 1 \right) \ln\left(\dot{c}_i L^{-1} + 1 \right) \qquad (9)$$

Basing on eq. (9) the mathematical funktion for the variation problem is defined as

$$\delta \left\{ \int_0^{\infty} \left[T \int_0^{t} \sigma \, d\tau - \sum_{i=1}^{k} \mu_i c_i; + \sum_{j=1}^{m} \lambda_j \left(\sum_{i=1}^{k} c_i \nu_{ij} - b_j \right) \right] dt \right\} \qquad (10)$$

Using the minimization of (10) the following set of differential equations for the reaction rates can be given

$$L \dot{c}_i = e^{A_i} - 1 \qquad i = 1...k \qquad (11)$$

The phenomenological coeffecient L is unknown usually, therefore system (11) can't be solved along the time coordinate. If a new variable ζ (process trajectory) is substituted into eq.(11) , $d\zeta = L^{-1} dt$, it follows

$$\frac{d \dot{c}_i}{d\zeta} = e^{A_i} - 1; \qquad b_j = \sum_{i=1}^{k} c_i \nu_{ij} \qquad j = 1...m \qquad (12)$$

The program package MAGIC solved the set of differential equations (12) by the Gear method with constant step widths for the distribution of the concentrations c_i along the process trajectory.Input dates were the pressure or volume of the closed systems, the initial concentrations of the input species and the thermodynamic functions of all involved species in the system. The calculations were carried out by using a database containing expertised information about more then 2500 individual substances.

Results and discussion

The reaction mechanism (Tab. 1) describes the conversion of 1,2-dichloroethane (Fig.1). The formation of HCl and stable products of hydrocarbons is caused by reactions of free radicals. Fig.2a presents the intermediate C/H/Cl compounds in the formation process of the decomposition products at T=2200 K. Their concentrations

rise up to a maximum and then decrease to zero with increasing reaction time. Especially the radical CH_2Cl is regarded to be the key radical in the first steps of the decomposition. The pathway to the products proceeds via the formation of chlorinated ethyne, ethene and methane - C_2HCl, C_2H_3Cl, CH_3Cl, CH_2Cl_2. At high temperatures the formation of C_3H, C_2, C_3 becomes significant. This is an indication of the importance of these radicals in the pyrolysis process.
Fig. 2b presents the concentrations (mole fraction) of the main reaction products determined by MAGIC for the pyrolysis of 1,2-dichloroethane at T = 2000 K. The main pyrolysis products and the relative order of their concentrations are in a quantitative agreement with the kinetic simulation by KINAL and with the experimental results.
Fig. 3 shows that the results of the calculations made by the program

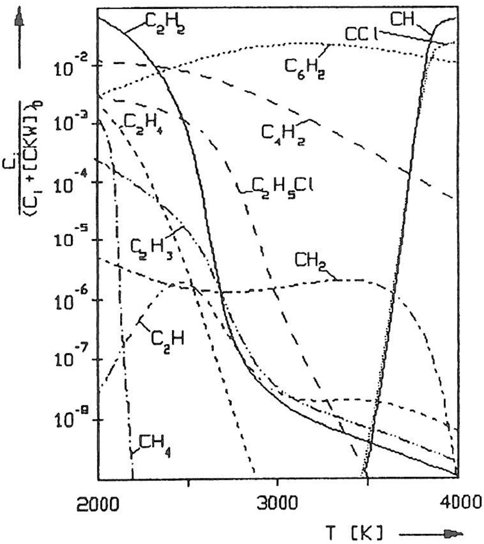


Fig. 1: Pyrolytic Change of 1,2-Dichloroethene: Stable Products and Radicals in Depedence on the Temperature (Reaction Time = 10^{-4} s) calculated by KINAL

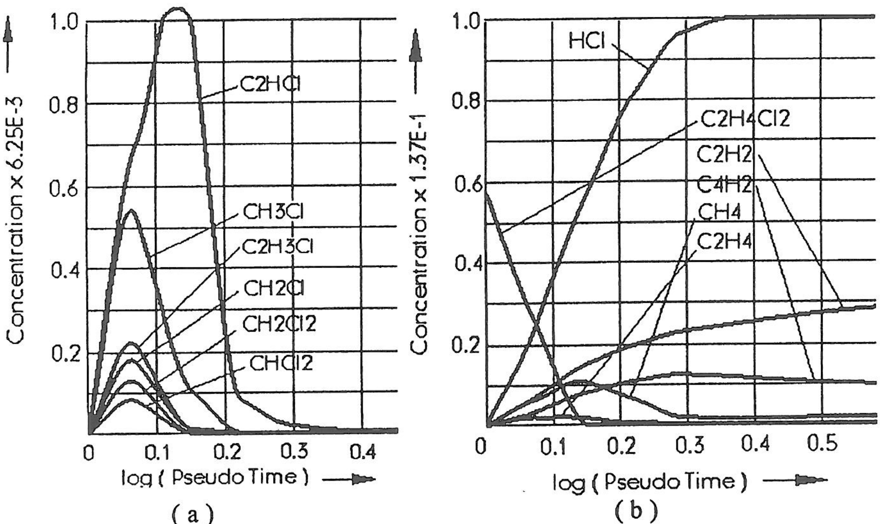
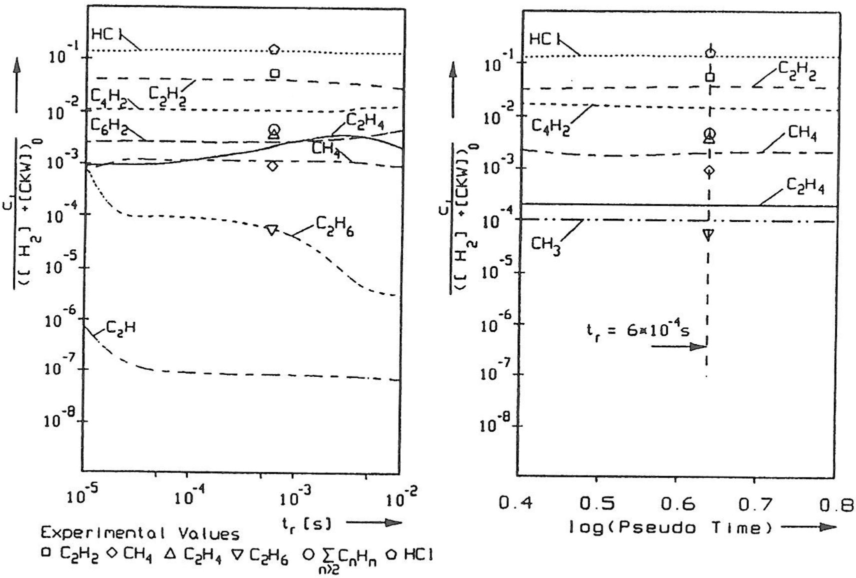


Fig. 2: Pyrolytic Change of 1,2-Dichloroethene at T=2000-2200 K.
(a): Intermediate Compounds in the Decomposition Process , (b):Stable Products, in Depedence on the Process Parameter ζ (Pseudo Time). Calculated by MAGIC



(a) (b)

Fig. 3: Concentrations of the main Species in a Hydrogen Plasma Jet (T=2000... 2200 K, p=10^5 Pa, Input 1.3 kgh^{-1} 1,2-Dichloroethane). Calculated by KINAL (a) and MAGIC (b), respectively.

MAGIC are generally in a good agreement with calculated results realized by the program KINAL as well as with the experimental results for the species HCl, C_2H_2, CH_4, C_2H_4.

The used method of modeling by the variation principle approach is also applicable to the modeling of plasma pyrolysis of other substancies. Especially this method may be succesful to obtain the reaction mechanism and intermediate compounds in komplex mixtures.

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