KINETICS OF THE NONTHERMAL PLASMACHEMICAL CONVERSION OF METHANE IN A BARRIER DISCHARGE

J. Rutkowsky, H. Drost, H.-D. Klotz
Akademie der Wissenschaften der DDR, Zentralinstitut für physikalische Chemie, DDR - 1199 Berlin, Rudower Chaussee 5

ABSTRACT

The plasmachemical decomposition of methane and its conversion to simple hydrocarbons in a barrier (corona) discharge have been investigated experimentally. The time dependence of product concentrations may be characterized by 2nd order kinetic equations of a successive reaction type. The macroscopic kinetic has been proved to be valid only for methane decomposition.

1. INTRODUCTION

A barrier or corona discharge is a low current electrical discharge through a barrier between the electrodes operated by an alternating voltage at pressures up to 1 atm. Though in barrier discharges (b.d.) only low current densities can be achieved its favourable nonthermal activation conditions for chemical reactions make the b.d. to a widespead tool in plasmachemistry. B.c. were applied mainly for ozone synthesis / 1 /, but in the last years with increasing tendency in performing synthesis of a great variety of chemical compounds, e.g. the propylene oxidation / 2 /, the CO/CO_2 conversion/3/, and the synthesis of high endothermic substances. There were also manyfold efforts in utilizing b.d. for cracking higher molecular hydrocarbons / 4 /. Most of product synthesis in a b.d. were performed from a practical point of view. In connection to that several efforts were made in the field of kinetics preferentially in methematical modelling the time dependence of product yields by a kinetical equation / 5 /. The following investigations were concerned with the decomposition of methane and the formation of secondary hydrocarbons in a b.d. It was the aim of these investigations to evaluate the time dependence as well of methane decomposition as of the formation of stable methane decomposition products and to model plasmachemical reaction course by means of a kinetical equation.

2. EXPERIMENTAL

The investigations were performed in a semi-barrier discharge reactor which as for its construction scheme can be regarded as identical with a device of standard ozonizer type. The reactor consists of two concentric cylindrical tubes of 120 mm length and an outer diameter of 31 mm. The inner steel tube is surrounded by a glass tube as barrier which is wrapped in a Al foil as second electrode. The discharge is maintained in the gap between the inner and the outer cylinder containing an active reactor volume of ca. 40 cm3. The reactor was operated at a alternating voltage of 50 Hz and amplitudes up 20 kV at a pressure which varied in the range of 250 to 750 Torr (0,33 10^5 to 1,00 10^5 Pa.) A scheme of the reactor is reproduced in Fig. 1. The discharge was operated at static conditions that is the reactor was closed up from the device after the methane pressure was adjusted. After switching off the discharge the product gas was filled into probes for analysis the product gas by gas chromatography.

3. RESULTS

3.1. Time dependence of methane pressure decay

The plasmachemical decomposition of methane in the b.d. were performed in dependence on discharge time resp. energy input and methane pressure. The decay of the methane concentration in the reactor in dependence on discharge time drawn in Fig.2 indicates to an exponential course, which can be expressed methematically by the initial relation

$$\frac{d}{dt}\left[CH_4\right]_t = -k_1 \quad \left[CH_4\right] \qquad (1)$$

from which by integration the following 1st order kinetic equation can be obtained

$$\left[CH_4\right]_t = \left[CH_4\right]_{t=0}\left(\exp - k_1 t\right) \qquad (2)$$

By means of equation (2) the decay of methane concentration in a barrier discharge with discharge time can be described satisfactorily. Deviations from equat. (2) occur at higher discharge times. They may be explained by the reformation of decomposed methane in secondary reactions with yields increasing preferentially at higher discharge times.

3.2. Synthesis of hydrocarbons

During methane decomposition in the b.d. several hydrocarbons as plasmachemical reaction products were formed with ethane and propane as main products and with propene, ethylene, acetylene a.o. in lower concentrations. The maximal concentrations of the 3 main products - ethane, propane, and butane - behave to each other in the ratio of 12•5: 2 (for a pressure of $3{,}32 \cdot 10^4$ Pa and a discharge voltage of 20 kV). When the concentrations of the 3 product are plotted against discharge time the resulting curves show with respect to the methane decomposition curve the typical course of successive reactions.

Such reactions may be kinetically expressed by the relation (in the case of ethane formation from methane):

$$\frac{d}{dt}\left[C_2H_6\right]_t = k_2\left[CH_4\right] - k_3\left[C_2H_6\right]_t \qquad (3)$$

in which the constants k_2 resp. k_3 refer to the formation of ethane from methane resp. the decomposition of ethane during the discharge. By solving the differential equation (3) for the time dependence of ethane formation the following 2nd order kinetic equation is obtained:

$$\left[C_2H_6\right]_t = \frac{\left[CH_4\right]_{t=0}\, k_1}{k_3 - k_1}\Big(\exp(-k_1t) - \exp(-k_3t)\Big) \qquad (4)$$

(with k_1 as the rate constant for the methane decomposition). The validity of equation (4) can be proved by a semiempirical method - by evaluating the 3 constants k_1, k_2, and k_3 from the experimental curve (fig. 2 and 3) and by calculating concentration values in dependence on discharge resp. reaction time according equation (4). The experimentally obtained ethane concentrations and the concentration values calculated by means of equation (4) in dependence on reaction time are shown from fig.3. The agreement between both curves seems to be especially for not too long discharge times satisfactorily.

3.3. Validity of macroscopic kinetics principle

The overall (macroscopic) behaviour of plasma chemical reactions has often been modeled by means of macroscopic kinetics / 6 /. The peculiarity of macroscopic" kinetics is the introduction of the specific energy E_v - the ratio of energy input E into the plasma and the active reaction volume in the plasma v - as an essential time independent the product formation derdermining parameter. The kinetic equation of macroscopic kinetics may be expressed as

$$\left[A\right]_{E_v} = \left[A\right]_\infty \left(1 - e^{-k_2 E_v}\right) \qquad (5)$$

If the quantity A in (5) is substituted by the concentration values of the formed products then equation (5) failed in obtaining a exponential dependence of product yields on specific Energy E_v. A exponential dependence can only be obtained for the concentration of the decomposed methane

$$\frac{\left[CH_4\right]_{E_v} - \left[CH_4\right]_\infty}{\left[CH_4\right]_{E_v}}$$

That is, macroscopic reaction kinetics is valid only for the plasmachemical methane decomposition or generally expressed - for plasmachemical first order reactions. This corresponds to the basic assumptions of macroscopic reaction kinetics which should be valid only for 1st order reactions. On the other hand the success in kinetic modelling of the time dependence of product formation in the b.d. indicates that it is principal possible to detect. kinetically 2nd order reactions even under nonthermal discharge conditions, a possibility, which was neglected by macroscopic kinetics.

3.4. Reaction mechanism

It can be assumed that the primary activation of methane molecules takes place preferently by electron impact leading to the formation of different CH_n radicals by H-atom abstraction

$$CH_4 + e \longrightarrow \left[\begin{array}{l} CH_3 + H \\ CH_2 + 2H \\ CH + 3H \end{array} \right. \qquad (6)$$

The formation of ethane molecules may be explained mainly by reactions of CH_3 radicals with CH_4 molecules

$$CH_3 + CH_4 \longrightarrow C_2H_6 + H \qquad (7)$$

A C_2H_6 formation via the reaction

$$CH_2 + CH_4 + W \longrightarrow C_2H_6 + W \qquad (8)$$

also may be assumed as probable with W as tube surface. The higher hydrocarbons like C_3H_8 resp. C_4H_{10} result from tertiary reactions of ethane molecules with CH_n radicals in the volume as well as on the tube wall.

4. CONCLUSIONS

1. By the nonthermal activation in a barrier (corona) discharge methane will decompose and a series of simple hydrocarbons, preferently ethane, propane, and butane are formed.

2. The methane decomposition on discharge time strongly follows an exponential kinetic 1st order equation whereas the time dependence of product concentrations may be characterized by 2nd order kinetic equations.

3. The macroscopic kinetic has been proved to be valid only for methane decomposition and failed in modeling product synthesis.

LITERATURE

(1) K.F. McTaggart "Plasma chemistry in Electrical Discharges" Elsevier Publishing Company, Amsterdam, London, New York 1967

(2) R. Weisbeck, D. Hüllstrung, Chemie-Ing.-Techn. 42 1302 (1970)
R. Weisbeck, Berichte der Bunsen-Gesellschaft 76 1147 (1972)

(3) E.A. Rubzowa, E.N. Eremin, in "Chimija i fizika niskotemperaturnoi plasmi" Moskov, State Univ.1971 p.243

(4) S.L. Lawrence, Chemical Engineering Progress 60 45 (1964)

(5) Iu.N. Shitnev, Iu.W. Filippov in "Chimija i fizika niskotemperaturnoi plasmi" Moskov, State Univ. 1971 p.251
R. Miquel, M. Chirol, Nem. Soc. chim. N 283 1677 (1963)

(6) H. Drost "Plasmachemie" Akademie Verlag, Berlin 1978

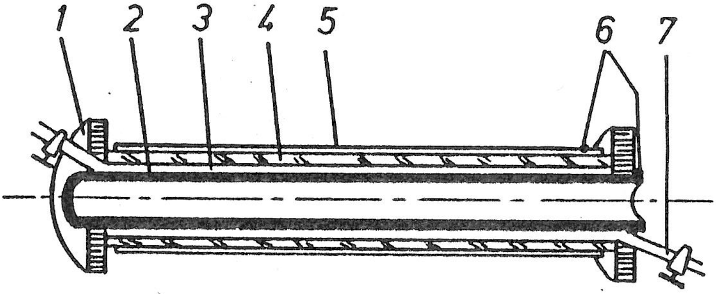

Fig. 1: Schematic of barrier discharge reactor
1 silicon rubber seal, 2 inner electrode, steel tube
3 reactor volume, 4 isolator (barrier), glass tube
5 outer electrode (Al foil), 6 electric leads,
7 gas in- and outlet

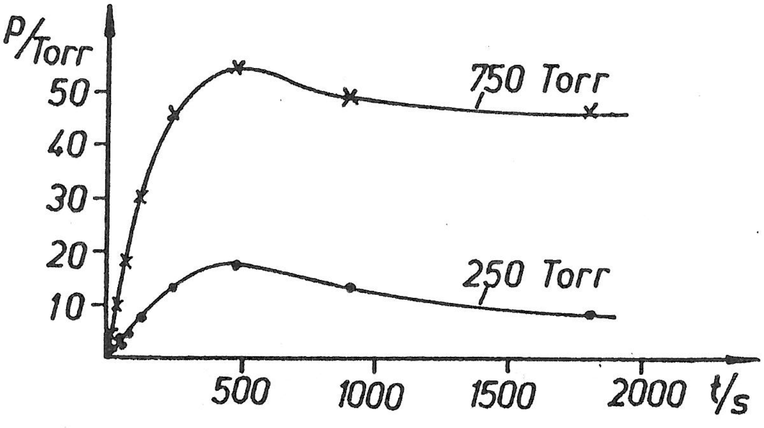

Fig. 3: Dependence of the ethane partial pressure on the time 750 Torr resp. 250 Torr methane initial pressure and at 20 kV discharge voltage.

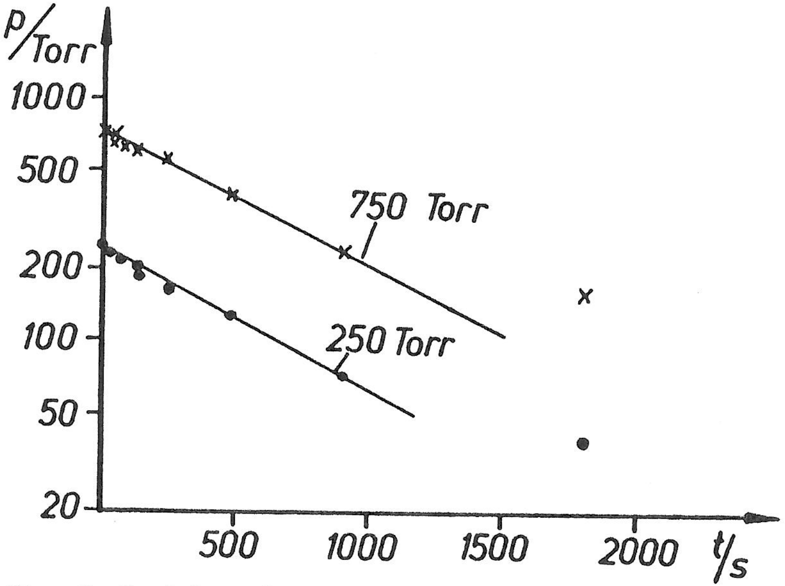

Fig. 2: Semi-logarithmic plotting of the methane partial pressure on the discharge time at 750 Torr resp. 250 Torr as methane initial pressure and at 20 kV discharge voltage

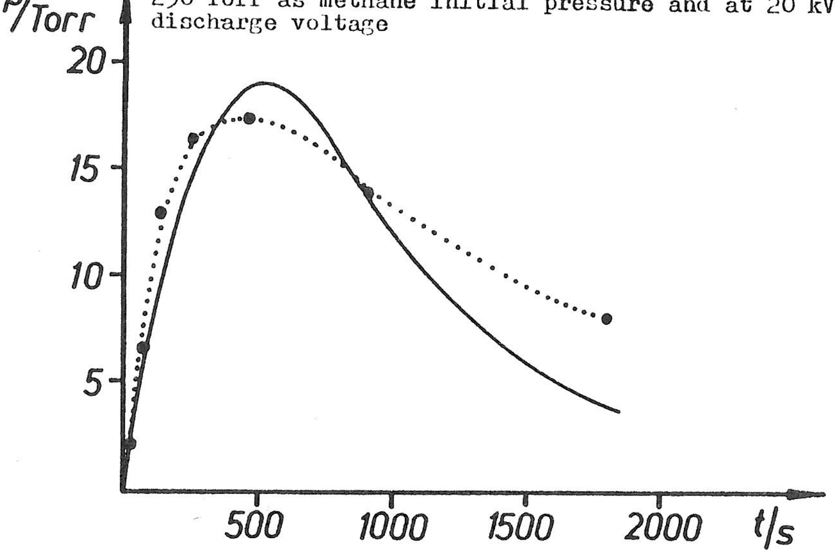

Fig.4 : Experimetal (dotted line)resp.calculated values(solid line) of ethane partial pressure in dependence on discharge time according to macroscopic kinetics