A KINETIC MODEL FOR THE ACTIVATION AND PLASMACATALYTICAL SENSIBILIZATION OF THE CO/H_2-CONVERSION TO HYDROCARBONS IN A GLOW DISCHARGE

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

ABSTRACT

The conversion of CO/H_2 mixtures to light hydrocarbons preferently to methane was investigated experimentally. The conversion degree depends on discharge time, CO/H_2 ratio, and pressure. The hydrocarbon formation will be kinetically explained by an ionic mechanism based on a successive H atom transfer. Due to plasmacatalytical sensibilization He resp.Ar additions cause a distinct increase of the conversion degree.

1. INTRODUCTION

Because of their favourable properties for nonthermal reaction activation glow discharges are preferently applicated in performing chemical reactions / 1 /. They are especially suitable for the activation of such reactions resp. product synthesis which couldn't be realized under the thermal conditions of a low temperature arc or jet plasma. A mixture of CO and H_2, the synthesis gas, is such a chemical system which oppose to be converted to other compounds, especially to hydrocarbons, (= H.C.) by means of thermal activation. The conversion of CO/H_2-mixtures to simple hydrocarbons in nonthermal electrical discharges was treated in several papers / 2 // 3 /. The attempts succeeded however in obtaining small conversion degrees of CO $\rightarrow$ H.C. especially to CH_4 as main product, and low partial pressures of formed H.C., which depend on the kind of the discharge, the reactions conditions (e.g. streaming or static system), the discharge parameters and the CO/H_2-ratio.

The following investigations are concerned with the plasmachemical CO/H_2-conversion to light H.C.under strong nonthermal activation conditions. It was the aim of the investigations to look for suitable operation conditions for high conversion degrees and for gaining new informations on the kinetics and the mechanism of the plasmachemical conversion process. Most attention was payed to the sensibilization of CO/H_2-conversion by means of gas additions based on plasma catalysis, that is to achieve by additional nonthermal reaction activation product concentrations,which exceed the equilibrium values.According to previous investigations on sensibilization in radiation chemistry and plasmacatalytical CH_4/N_2-conversion to hydrazine / 4 /, the plasmacatalysis should be performed by means of additions of He and Ar gas to the original CO/H_2-mixture.

2. EXPERIMENTAL

The investigations were performed on a experimental device consisting of 2 equal discharge glass tubes T_1 and T_2 (Fig.1). T_1 was operated under static conditions and served as reactor for the synthesis of stable products, which were extrated by a Toepler-pump for gaschromatographic analysis. Tube T_2 served as source for mass spectrometric analysis of the intermediate ionic species formed during discharge operation by means of a double focussing so called plasma mass spectrometer. T_2 worked under flowing gas conditions. Electrodes (cold metallic cylinders) and discharge conditions were chosen in order to ensure the formation of an utmost high cathode fall, the important presupposition for establishing high activation conditions. The discharge was operated by a high voltage direct current generator. The operation conditions varied in the range of 600 - 1000 V and 50 - 75 mA at neutral gas pressures of 13 - 400 Pa.

3. RESULTS

The obtained results may be summerized as follows:

- Unter the nonthermal conditions of a glow discharge CO/H_2-mixtures will be converted to simple H.C. As main product methane was observed. The second important product, ethane, appeared in concentrations of an order of magnitude smaller than those of methane. From other H.C. products like C_2H_2, C_2H_4, C_3H_8 and C_4H_{10} only traces could be detected. Furthermore small amounts of CO_2, H_2O, O_2, and CH_2O were mass spectrometrically identified as reaction products too.
- The conversion degree α of $CO \rightarrow CH_4$ strongly depends on discharge time resp. energy input and CO/H_2 concentration ratio. The highest conversion degrees in the order of 12% were obtained at medium discharge times of 100 s and at CO/H_2-concentration ratios of 10%, that is at a high excess of H_2. The methane content in the product gas does'nt exceed 3 %.
- The conversion degree α $CO \longrightarrow CH_4$ increases proportionally with the neutral gas pressure independently of the CO/H_2-concentration ratio (Fig. 2).
- Additions of He resp. Ar as plasmacatalytical acting gas cause a manifold increase of the conversion degree, in the case of He values were achieved which were up to 7 times greater than for He free conditions (Fig. 3).

4. DISCUSSION

The experimental results mainly the methane formation from CO/H_2-mixtures may be explained by a sequence of ion molecule reactions based on a successive H atom transfer to CO^+-containig molecules. The initial step of the mechanism is the CO^+-ion formation by electron impact or preferently by charge transfer processes with H^+, H_2^+ and H_3^+-ions, respectivly. Starting with the CO^+-ion, successive reactions with H_2 molecules lead to product ions in the sequence of CHO^+, CH_2O^+, CH_3O^+ and CH_4O^+. These product ions may react simultaneously with CO-molecules by which in dependence on the stage of hydrogeneration C/H-radical-ions were formed. The mechanism can be characterized in detail as follows:

$$
\begin{array}{l}
CO + \left\{\begin{array}{l} e \\ H^+ \\ H_2^+ \end{array}\right. \longrightarrow CO^+ \\
\qquad\qquad\qquad \downarrow H_2 \\
\qquad\qquad\qquad CHO^+ + CO \longrightarrow CH^+ + CO_2 \\
\qquad\qquad\qquad \downarrow H_2 \\
\qquad\qquad\qquad CH_2O^+ + CO \longrightarrow CH_2^+ + CO_2 \\
\qquad\qquad\qquad \downarrow H_2 \\
\qquad\qquad\qquad CH_3O^+ + CO \longrightarrow CH_3^+ + CO_2 \\
\qquad\qquad\qquad \downarrow \\
\qquad\qquad\qquad CH_4O^+ + CO \longrightarrow CH_4^+ + CO_2
\end{array}
\tag{1}
$$

The different product ions, the O-containing ions as well as the C/H-radical ions will be neutralized on the negatively charged tube walls. The low pressure in the tube favours the neutralization reactions on the wall for which the probability is higher by a factor of 10^4 compared with volume reactions. In such neutralization reactions on the walls O atoms may be abstracted and react subsequently with hydrogen to water molecules resp. C/H-radicals may recombine to higher H.C. The presented reaction scheme is verified by several experimental facts:

- All of the ionic species occurring in the reaction scheme, the O-containing ions as well as the C/H radical ions have been idenfified by plasma spectrometry.
- The listed ion molecule reactions are well known from similar reaction conditions and are characterized by high cross sections / 5 /.
- The presence of CO_2 as well as of H_2O molecules in the discharge tube has been identified mass-spectrometrically.
- The time denpendence of CH_4- and C_2H_6-molecule formation indicates, that C_2H_6 molecules were formed not only via methane but also via primary C/H radicals.

The occurrence of a plasmacatalytic effect in sensibilization of the CO/H_2 conversion to H.C. by additions of He and Ar to the reaction system may be interpreted as an approvement of the proposed mechanism. Due to the presence of He or Ar atoms in the discharge additional charge transfer resp. Penning ionization processes will be initiated, from which additional CO^+ ions arise

$$
\left.\begin{array}{l} He^+ \\ He\ (2^3S) \end{array}\right\} + CO \longrightarrow CO^+ + He \tag{2}
$$

If He^+ ions react first via charge transfer processes with H_2-moleculs, then CO^+ ions will be formed by subsequent charge transfer processes with H_2^+ resp. H^+ ions. The distinct sensibilizing effect caused by excited or ionized He resp. Ar atoms in the plasma is the result of the much higher cross sections of charger transfer-reactions compared to that of electron impact ionization. So by the round-about-way of He resp. Ar ionization finally more CO^+-ions will be formed than by the direct electron impact ionization.

5. CONCLUSIONS

1. CO/H_2 mixtures will be converted to light hydrocarbons, preferently to methane, by nonthermal activation in a glow discharge.

2. The conversion degree of CO/H_2 to methane and the methane partial pressure depend on discharge time resp. energy input, CO/H_2 ratio, and discharge pressure.

3. The CO/H_2 conversion to hydrocarbons will be kinetically explained by an ionic-mechanism based on a successive H atom transfer to CO^+-containing molecules.

4. The conversion degree to methane will be distinctly increased by a plasmacatalytical sensibilization effect due to additions of He resp. Ar to the CO/H_2 system.

REFERENCES

(1) H. Suhr, Angewandte Chemie 84, 876 (1972)

(2) B.-D. Blaustein, Y.C. Fu, "Techniques of Chemistry", Vol. I Part II B, edited by A. Wissberger (New York, London, Sydney, Toronto, 1971) p.91

(3) B.-D. Blaustein, W.A. Steiner, Y.C. Fu, J. Phys. Chem., 76, 2941 (1972)

(4) H. Drost, H.-D. Klotz, 3rd International Symposium on Plasma Chemistry, Limoges, (1977) G. 2. 7.

(5) L.I. Wirin et al, "Ion-Molecule-Reactions in Gases" (russ.) (Akademia Nauk, Moscow, 1979)

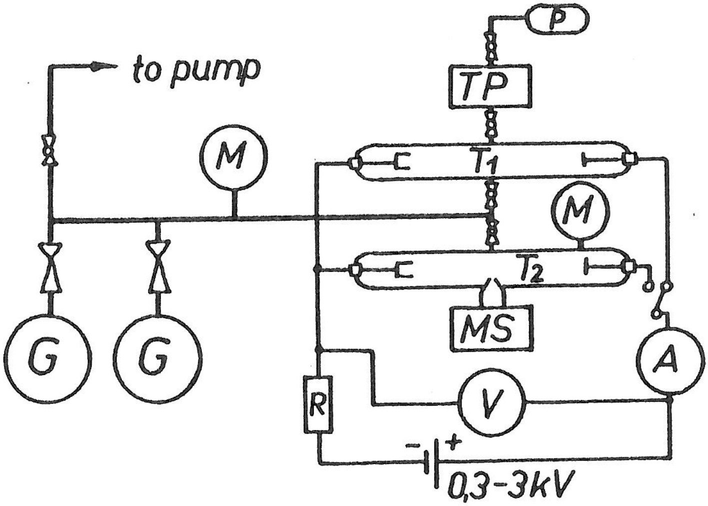

Fig. 1 : Schematic drawing of the apparatus. T - discharge tube, MS - mass spectrometer, TP - Toepler pump, P - product gas probe, G - gas reservoir, M - manometer.

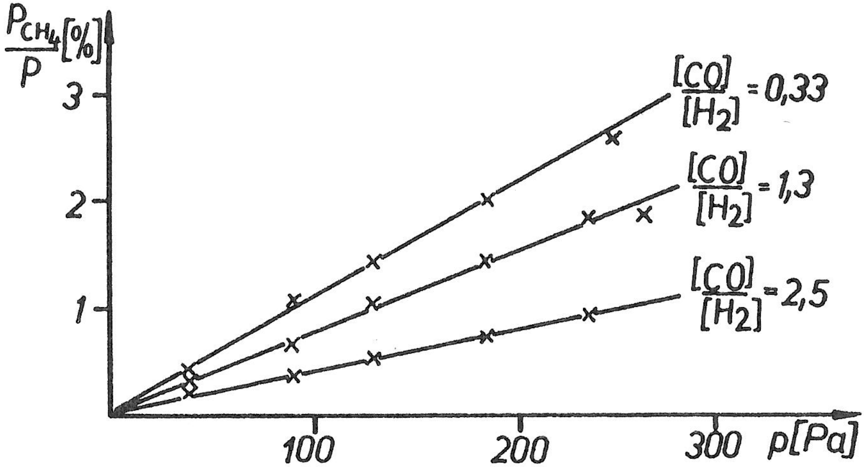

Fig. 2 : Partial pressure of formed methane versus discharge pressure, of different ratios of CO/H_2 as parameter. Discharge time 100 s, discharge current 75 mA.

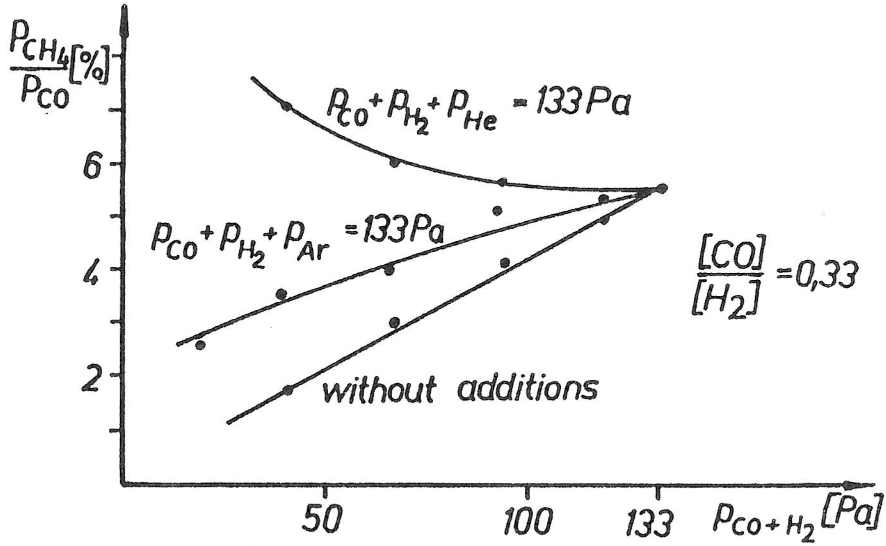

Fig. 3: Influence of He resp. Ar additions on the conversion degree of $CO \rightarrow CH_4$ in the CO/H_2 glow discharge. Discharge time 100 s, discharge current 75 mA.