

PYROLYSIS OF ACETYLENE: PRIMARY PRODUCTS, INDUCTION PERIOD AND INFLUENCE OF IMPURITY

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Introduction

The formation of C_2H_2 and its further transformations are regarded as important steps in the pyrolysis and combustion of several hydrocarbons. C_2H_2 and products of its reactions at high temperatures are believed to play an important role in formation of PAHs and carbons. The mechanism of the pyrolysis, especially its initiation, is the subject of intense controversy. The models proposed encompass different ideas: formation of a symmetrical C_2H_2 diradical¹, disproportionation of two C_2H_2 molecules to form vinyl and ethynyl radicals², a radical mechanism dominated by C_4H_3 ³, isomerisation of C_2H_2 to form vinylidene^{4,5}, initiation of a radical chain by acetone, present as an impurity⁶ and formation of a symmetrical C_4H_4 diradical⁷. The theories rest on a rather limited experimental foundation; most of experimental studies were done between 1950 and 1980. More recent studies do not provide all the evidence needed to distinguish between the various mechanisms. This study aims to provide experimental data on the primary products of acetylene pyrolysis.

Experimental

The experiments were carried at temperatures from 914 K to 1038 K, pressures from 4.70 kPa to 44.03 kPa and residence times between 4 ms and 55 ms. The conversion of acetylene to observed products was always less than 0.2%. Two quartz flow reactors were used: one tubular ($r=0.8634$ mm) and one annular, both of them 42 cm long. The large length-to-radius ratio was maintained in order to avoid effects of incomplete radial heat transfer. The pressure was controlled and monitored with a precision better than ± 35 Pa. The temperature was controlled, permitting variations with respect to time of less than ± 0.5 K. The temperature profile at 20 points along the reactor had deviations of ± 5 K from the programmed plateau value.

Purified acetylene (Canox, <7000 ppm acetone, <400 ppm of other hydrocarbons) was used,

without dilution. Impurities having boiling points above 195 K were removed in a cold trap. After purification the concentration of acetone dropped to 20-50 ppm, and the amount of all other impurities was estimated to be 30-60 ppm.

The gaseous products were analyzed using gas chromatography and infrared or mass spectrometry. In most cases a Porapak gas chromatograph column was used to separate gaseous products. Detectability limits were in the order of 10^{-9} mol/L. In order to verify the results columns packed with Carbowax M-20 and with 10% squaline on Chromosorb were used. In some cases, depending on the concentrations of the products, gas samples for IR and MS were frozen and the excess of acetylene was removed by distillation.

Results and Discussion

Preliminary experiments showed that two gaseous products were formed, as well as a black, carbon-rich product at the wall of the reactor. The gaseous products were identified as vinylacetylene (VA) and benzene (B). The [VA]/[B] ratio was found to be 5.40 at 6.10 kPa and 963 K and decreased to 1.99 at 39.99 kPa.

This behaviour was confirmed by the results obtained at 914 K and 1014 K. The [VA]/[B] ratio was found to be temperature dependent, increasing with increasing T. This effect was more pronounced at lower pressures.

Due to the reactor geometry, the pressures at the inlet and outlet of the reactor differed by 5% at 39.99 kPa, and by a greater fraction at lower pressures. This introduced uncertainty regarding the existence of an induction period as well as regarding the reaction order.

Assuming ideal gas behaviour, the residence time, τ , for gas phase reactions is given by

$$\tau = P r^2 \pi L_{\text{eff}} / (F R T_{\text{eff}}) \quad (1)$$

where P, R, r , L_{eff} , T_{eff} and F are gas pressure, gas constant, reactor radius, effective reactor length,

temperature and molar flow rate, respectively. Since P is not a linear function of the distance along the reactor, it would not be correct to use an arithmetic mean value. As a consequence, classical methods to determine the reaction order are not adequate. Instead, we have adopted the approach that the pressure drop modifies the measured values of the product concentrations, or partial pressures, p . The yield of product (e.g. VA) is then given by

$$dp_{VA}/dt = (n_{VA}/n)(dP/dl)(dl/dt) + V\nu_{VA}k(P/n)[C_2H_2]^N \quad (2)$$

where N denotes reaction order, n the number of moles and t the time. (dP/dl) is the pressure gradient at axial position, l , and can be calculated from the integral form of Poiseuille's equation, and (dl/dt) is the flow velocity which is quantified by means of the molar flow rate. With a single assumption that the total number of moles, n , does not change with time, which can be justified by the small conversion of C_2H_2 ($\approx 0.2\%$), the integration of Eqn. (2) for a given temperature yields

$$p_{VA} = a Q, \quad \text{where} \quad (3)$$

$$a = \nu_{VA} k \pi^2 r^6 / [8 \eta (RT)^{N+1} (N+3)] \quad (4)$$

η - coefficient of viscosity at a given T

$$Q = (P_0^{N+3} - P_L^{N+3}) / F^2 \quad (5)$$

P_0 and P_L are pressures at the inlet and outlet of the reactor, respectively. For constant temperature the plot of p as a function of Q should give a straight line, for the correct value of N . In other words, using the deviation from linearity as a criterion and by incrementing values of N , an iterative method can be used to determine the reaction order. If the value of N is overestimated or underestimated, a deviation from linearity occurs leading eventually to the overlapping of p or Q values. In our case, the method was insensitive within increments less than 0.2. The value of the rate constant, k , can be calculated from the slope a . This procedure gave the values $N_{VA} = 1.9$ and $N_B = 2.7$ as best fits; the orders were found to be independent of T . Rounding these orders to two and three, respectively, the values for preexponential factors and activation energies were estimated, $A_{VA} = 1.4 \times 10^{13} \text{ L}/(\text{mol s})$, $E_{VA} = 233 \text{ kJ/mol}$, and $A_B = 1.1 \times 10^{12} \text{ L}^2/(\text{mol}^2 \text{ s})$, $E_B = 175 \text{ kJ/mol}$. Assuming that VA and B are the only major products the data were used to calculate the parameters for C_2H_2 decomposition, at 101 kPa,

$$A = 2.6 \times 10^{11} \text{ L}/(\text{mol s}), \quad E = 194 \text{ kJ/mol}$$

In all the experiments a thin layer of carbonaceous deposit was formed on the entire length of the reactor wall.

In order to investigate the influence of acetone, (AT) purified and nonpurified C_2H_2 was pyrolysed. The presence of AT resulted in four-fold increases in the yields of both products, as well as increases in activation energies of 30% for VA and 50% for B. These experimental facts indicate the important role that AT can play in the initiation of C_2H_2 decomposition.

The results obtained with purified C_2H_2 showed an induction period of 20 ms for both products at 7.53 kPa, and induction periods of 20 ms for VA and 30 ms for B at 4.85 kPa. There was no evidence of an induction period when AT was present under the same conditions.

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