An induction period in the pyrolysis of acetylene

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Acetylene was pyrolysed in a flow system between 854 and 970 K, at pressures between 27 and 127 Torr and at residence times between 8 and 1520 ms. Both vinylacetylene and benzene were observed to be primary products, but secondary processes removed vinylacetylene and formed benzene. The orders for the steady-state rates of formation of vinylacetylene and benzene were measured to be 1.8 ± 0.1 and 2.4 ± 0.1 , respectively. The corresponding rate constants were found to be, $\ln(k_{VA}/L \text{ mol}^{-1} \text{ s}^{-1}) = -(165 \pm 11) \text{ kJ}$ mol⁻¹/RT + (22.7 ± 1.5) and $\ln(k_B/L^{1.4} \text{ mol}^{-1.4} \text{ s}^{-1}) = -(100 \pm 9) \text{ kJ} \text{ mol}^{-1}/RT$ + (15.6 ± 1.1). Induction

 $\text{mol}^{-1}/RT + (22.7 \pm 1.5)$ and $\ln(k_{\text{B}}/\text{L}^{1.4} \text{ mol}^{-1.4} \text{ s}^{-1}) = -(100 \pm 9)$ kJ mol⁻¹/ $RT + (15.6 \pm 1.1)$. Induction periods were observed for the first time at these conditions, providing evidence that a free radical process dominates. The order of the initiation reaction was shown to be two. The temperature dependence of the product of the rate constants for the bimolecular, initiation reaction and the termination reaction was determined to be, $\ln(k_ik_t/\text{L}^2 \text{ mol}^{-2} \text{ s}^{-2}) = -(261 \pm 7)$ kJ mol⁻¹/ $RT + (53.1 \pm 1.0)$.

1. Introduction

Acetylene is believed to be a precursor of polycyclic aromatic hydrocarbons (PAHs) and soot in the pyrolysis and combustion of various hydrocarbons.^{1–5} The first experiment on the pyrolysis of acetylene was performed by Berthelot in 1866.⁶ Various devices have been used to study this reaction, including static reactors,^{7,8} flow reactors^{8,9} and shock tubes.^{10–17}

Several mechanisms have been proposed. The mechanism at temperatures above 1500 K is believed to be a free radical process.^{10,16} However, the mechanism below 1500 K is still the subject of sharp controversy. Free radical mechanisms were proposed¹⁸⁻²¹ because of observations of autoacceleration and because of the inhibition of the reaction by nitric oxide, a known scavenger of free radicals. Several, different initiation reactions have been suggested. Minkoff²² proposed that one of the triple bonds in an acetylene molecule could rupture to form a triplet, which then propagated a polymerization reaction. Back¹⁸ suggested that the initiation reaction was a bimolecular disproportionation between two acetylene molecules to form vinyl and ethynyl radicals. Other workers^{10,19,21,23} suggested a bimolecular initiation reaction forming C₄H₃ and a hydrogen atom. Colket et al.²⁰ suggested that the reaction was initiated by acetone, an impurity in acetylene.

Because some free radical mechanisms predicted slower rates of reaction than those observed experimentally, Duran *et al.* (DAC)²⁴ proposed a molecular mechanism involving vinylidene, H₂CC, providing three supporting arguments. Firstly, *ab initio* calculations predicted that the heat of formation of vinylidene was only 167 kJ mol⁻¹ greater than that of acetylene.^{25,26} Secondly, their studies²⁷ of the thermal reactions of acetylene with benzene and toluene were interpreted to reveal that the reactions were additions, instead of radical displacements. Finally, vinylidene had previously been suggested to participate in the high-temperature decomposition of methylenecyclopropane.²⁸ To interpret the observations of autoacceleration and the inhibition of the reaction by nitric oxide, DAC's molecular mechanism was further developed by Kiefer and Von Drasek.^{29,30} Published experimental results are limited and are subject to interference by secondary and even tertiary reactions, so neither proposed mechanism could be eliminated. Study of the pyrolysis of acetylene at low conversions should provide crucial information regarding the mechanism.

When a free radical reaction starts, it takes a short time for free radicals to be formed and to reach their steady concentration. This period of time is usually called the induction period. Induction periods were observed in free radical polymerizations in the liquid phase using the viscosity method,³¹ the rotating-sector technique³² and the emulsion technique.³³ A mathematical theory was proposed by Come³⁴ for induction periods in the pyrolysis of hydrocarbons. Induction periods have been observed in the pyrolysis of ethane,³⁵ ethylene,³⁶ neopentane,^{37,38} acetone³⁹ and 1,2-dichloroethane.⁴⁰ Such induction periods were usually observed in flow systems.

An equation was derived for the rate of formation of methane in neopentane pyrolysis in a plug flow system.³⁸ A similar equation applies to other cases where the key radicals are removed in a bimolecular, chain termination.

$$[\mathbf{P}]/t = [(b_{\mathbf{P}}/t)\ln\{[1 + \exp(a_{\mathbf{P}}t)]/2\} - a_{\mathbf{P}}b_{\mathbf{P}}/2](1 - c_{\mathbf{P}}t) \quad (E1)$$

Here, [P] is the concentration of a product leaving the reactor; t, the residence time of gases in the reactor; $a_p b_p$ equals $2R_p^{ss}$ where R_p^{ss} is the steady-state rate of product formation; a_p equals $4(R_i k_i)^{1/2}$ where R_i is the initiation rate; k_t , the termination rate constant; and c_p , a parameter associated with secondary reactions. The relation between the induction period, τ , and the parameter, a_p , was derived as eqn. (E2),³⁴ assuming the termination step was second order.

$$\tau = 1/(k_i k_t [C_2 H_2]^n)^{1/2} = 2 \ln 2/a_p$$
(E2)

Here, k_i is the rate constant for the initiation reaction and n is the order of the initiation reaction.

Vinylidene was proposed to be a key intermediate in the molecular mechanism. The induction period caused by the delay in establishing the steady-state concentration of vinylidene should be its lifetime, $3.5 \ \mu s$, a recent experimental result by Levin *et al.* using coulomb explosion imaging techniques.⁴¹ This is too fast to be observed in a flow system. Therefore, the

observation of an induction period at low temperatures would be an excellent method to distinguish between a free radical mechanism and a molecular mechanism.

In the present work, we will search for an induction period of a few milliseconds at very low conversions.

2. Experimental

Acetylene was pyrolysed in a flow system, described elsewhere.⁴² Cylindrical quartz tubes (Quartz Scientific, Inc.) of 28 cm length and 0.969 mm, 1.96 mm and 3.96 mm internal diameters were used as reactors. Acetylene (Canox, <30000 ppm acetone) was passed through an isopropanol/dry ice trap, which reduced the mole fraction of impurities to less than 120 ppm of acetone, less than 270 ppm of ethane, less than 250 ppm of propane and less than 80 ppm of propylene. But-1-ene (Matheson, C. P.), acetone (Fisher, A. R.) and benzene (Fisher, A. R.) were used to prepare calibration mixtures to determine the concentrations of products and acetone. Here, but-1-ene was used to calibrate vinylacetylene (VA) due to the lack of suppliers of vinylacetylene. A gas chromatograph (Tracor 550) with a Hayesep D column (3.1 m, Alltech) and a flame ionization detector was used to analyze products at a temperature of 210 °C. Nitrogen (extra dry, Praxair) was used as carrier gas. To estimate the systematic error caused by calibration, GC sensitivities of but-1-ene and buta-1,3-diene were compared; the former sensitivity was 6% higher than the latter value. Therefore, the systematic error resulting from the replacement of vinylacetylene by but-1-ene for calibration should be very small.

All reactors were immersed in concentrated HNO₃ overnight to remove organic and inorganic impurities. Then, the reactors were washed with a 25% HF solution, rinsed with distilled water and dried. Carbon deposited in the reactor was burned off between injections by flowing purified air through the reactor at 200 Torr. Injections were made when the acetylene had flowed for only 5 min, so as to limit any build-up of carbon, which had been found to inhibit the gas phase reaction in a previous study.⁴²

3. Results

3.1. Observation of induction periods for the formation of vinylacetylene and benzene

Acetylene was pyrolysed in a flow system between 854 and 970 K, at pressures between 27 and 127 Torr and at residence times between 8 and 1520 ms. Only vinylacetylene and benzene were observed as products in these conditions. The flow rates of acetylene into the reactors and the diameters of the reactors were varied to attempt to detect an induction period in the formation of vinylacetylene and benzene. The residence time of gas in the reactor was calculated from the reactor temperature and volume, and from the gas pressure and flow rate. The average rates of formation of vinylacetylene (R_{VA}) and benzene (R_B) were calculated by dividing their concentrations at the reactor exit by the residence times. Conversions were calculated to be in a range between 0.0022% and 1.4%. Reactors with smaller inner diameters were used at high pressures or high temperatures.

Fig. 1 shows the average rates observed for vinylacetylene and benzene at 27 Torr and 935 K in a 3.96 mm id reactor at residence times between 0.027 and 0.39 s. At residence times greater than 0.2 s, the rates of formation of vinylacetylene and benzene were almost independent of the reaction time; this behavior would be characteristic of a primary reaction occurring with the concentrations of intermediates at their steady-state values. At shorter residence times, the rates of product formation were much less. At the shortest residence



Fig. 1 Dependence of the rates of formation of vinylacetylene and benzene on the residence time at 27 Torr and 935 K in a 4 mm id reactor; (\blacksquare) vinylacetylene; (\blacklozenge) benzene; solid curve, non-linear least-squares fit of eqn. (E1) to the data for vinylacetylene; dotted curve, non-linear least-squares fit for benzene.

time, the rates of formation of vinylacetylene and benzene were only 24% and 21%, respectively, of their values at 0.4 s. This behavior is characteristic of an induction period. The increases in the rates of formation for vinylacetylene and benzene were almost parallel to each other; indicating that their induction periods were similar.

Fig. 2 shows typical induction periods observed at 68 Torr and 936 K in a 1.96 mm id reactor. The rate of formation of vinylacetylene increased with increasing residence time to a maximum value, and then gradually fell off. On the other hand, the rate of formation of benzene increased with the residence time to a shoulder value, and then continued to increase more gradually.

3.2. Results of fitting the induction periods for vinylacetylene and benzene

Eqn. (E1) was fitted to the data for vinylacetylene and benzene by non-linear least squares.⁴³ Fig. 1 and 2 show examples of the fitted curves. Table 1 lists the values of the parameters obtained from the fits. Quoted uncertainties are standard deviations. The values of the induction period, τ , obtained from the vinylacetylene data and from the benzene data agreed within 9% in most cases. There were differences in a few cases at low pressures because of the larger errors in the benzene data, associated with the much smaller peaks for benzene. The steady state rates obtained for vinylacetylene were greater than those obtained for benzene. The parameters, c, obtained from the secondary processes for vinylacetylene and for benzene were similar in absolute magnitude, but opposite in sign.



Fig. 2 Dependence of the rates of formation of vinylacetylene and benzene on the residence time at 68 Torr and 936 K in a 2 mm id reactor; (\blacksquare) vinylacetylene; (\blacktriangle) benzene; solid lines, non-linear least-square fits of eqn. (E1) to the data.

 Table 1
 Parameters of the progress curves for vinylacetylene and benzene obtained by nonlinear least-squares fits of eqn. (E1) to experimental data

<i>T/</i> K	<i>P/</i> Torr	Reactor id/mm	$ \frac{\tau_{VA}}{s} $	$rac{ au_{B}}{s}$	$\frac{R_{\rm VA}^{\rm ss}}{10^{-7}}$ mol L ⁻¹ s ⁻¹	$\frac{R_{\rm B}^{\rm ss}}{10^{-7}}$ mol L ⁻¹ s ⁻¹	$c_{\rm VA}/{\rm s}^{-1}$	$c_{\mathbf{B}'} \\ \mathbf{s}^{-1}$
970	53	1.96	0.035 ± 0.002	0.038 ± 0.006	67.5 ± 1.5	8.5 ± 0.5	0.44 ± 0.04	-1.03 ± 0.16
970	36	0.969	0.049 ± 0.005	0.086 ± 0.018	30.1 ± 1.1	4.03 ± 0.25	а	a
938	126	0.969	а	a	195 ± 8	65 ± 5	а	a
936	69	1.96	0.045 ± 0.003	0.041 ± 0.008	63 ± 3	12.8 ± 1.1	0.30 ± 0.09	-0.55 ± 0.27
934	52	3.96	0.056 ± 0.007	0.057 ± 0.006	40.6 ± 1.7	7.0 ± 0.3	0.34 ± 0.06	-0.37 ± 0.07
934	34	3.96	0.096 ± 0.012	0.072 ± 0.006	20.8 ± 1.3	2.33 ± 0.10	0.36 ± 0.07	-0.60 ± 0.09
935	27	3.96	0.121 ± 0.005	0.151 ± 0.014	11.5 ± 0.2	1.76 ± 0.07	а	a
895	60	3.96	0.118 ± 0.008	0.105 ± 0.003	22.7 ± 0.8	6.9 ± 0.1	0.20 ± 0.04	a
854	120	3.96	0.121 ± 0.003	0.121 ± 0.009	28.1 ± 2.0	16.9 ± 0.4	0.090 ± 0.001	а
^a There	e was ins	ufficient data	to reliably obtain	the missing paran	neters.			

The orders of the parameters were calculated from their pressure dependences at 934–936 K. Fig. 3 shows an order plot for the induction period, τ . The order for τ_{VA} was -1.09 ± 0.07 . The order for τ_B was -1.2 ± 0.3 , and the order for the combination of τ_{VA} and τ_B was -1.1 ± 0.1 . In determining these orders, individual points were given weights proportional to the inverse squares of their fractional standard deviations. All these values are consistent with an order of -1, indicating that the value of *n* (the order of the initiation reaction) in eqn. (E2) is 2. Fig. 4 shows that the order for the formation of vinylacetylene, R_{B}^{ss} , was 2.4 ± 0.1 . The parameters, c_{VA} and c_{B} , were found to be almost independent of the pressure.

Arrhenius plots for $k_i k_t (=(\tau [C_2H_2])^{-2}$ from eqn. (E2)) are shown in Fig. 5. Similar parameters (E3)–(E5) were derived from different sets of data.

$$\ln(k_i k_t / L^2 \text{ mol}^{-2} \text{ s}^{-2})_{VA} = -(268 + 8) \text{kJ mol}^{-1} / RT + (54.1 + 1.1)$$
(E3)

 $\ln(k_i k_t/L^2 \text{ mol}^{-2} \text{ s}^{-2})_{\rm B} =$

 $-(231 \pm 34)$ kJ mol⁻¹/RT + (49.2 ± 4.4) (E4)

 $\ln(k_i k_t/L^2 \text{ mol}^{-2} \text{ s}^{-2})_{VA+B} =$

$$-(261 \pm 7)$$
kJ mol⁻¹/RT + (53.1 ± 1.0) (E5)

Here, eqn. (E5) was obtained from the data for both vinyl-acetylene and benzene.



Fig. 3 Dependence of the induction period, τ , on the acetylene concentration at 934–936 K; (\blacksquare) vinylacetylene; (\triangle) benzene; solid line, weighted least-squares fit to the data for both vinylacetylene and benzene.

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Arrhenius plots for $k_{VA}(=R_{VA}^{ss}/[C_2H_2]^2)$, and $k_B(=R_B^{ss}/[C_2H_2]^{2.4})$ are shown in Fig. 6. Here the order for R_{VA}^{ss} was rounded to 2, but the order for R_B^{ss} was kept as a fraction. Eqns. (E6) and (E7) were obtained from the data on vinyl-acetylene and benzene, respectively.



Fig. 4 Dependence of the steady-state rates, R^{ss} , on the acetylene concentration at 934–936 K; (\blacksquare) vinylacetylene; (\blacktriangle) benzene.



Fig. 5 Arrhenius plot of $k_i k_t$; (\blacksquare) vinylacetylene; (\triangle) benzene; solid line, weighted least-squares fit to the data for both vinylacetylene and benzene.



Fig. 6 Arrhenius plots for $k/L^n \mod^{-n} s^{-1}$ (n = 1 for vinylacetylene, and 1.4 for benzene), the effective rate constants in the steady-state regime; (\blacksquare) vinylacetylene; (\blacktriangle) benzene.

$$\ln(k_{\rm VA}/\rm L\ mol^{-1}\ s^{-1}) =$$

 $-(165 \pm 11)$ kJ mol⁻¹/RT + (22.7 ± 1.5) (E6)

 $\ln(k_{\rm B}/{\rm L}^{1.4} {\rm mol}^{-1.4} {\rm s}^{-1})_{\rm B} =$

$$-(100 \pm 9)$$
kJ mol⁻¹/RT + (15.6 ± 1.1) (E7)

Fig. 7 shows the Arrhenius plots for the parameters, $c_{\rm VA}$ and $c_{\rm B}$. The following equations were derived,

$$\ln(c_{VA}/s^{-1}) = -(95.4 \pm 9.3)\text{kJ mol}^{-1}/RT + (11.1 \pm 1.2)$$
(E8)

$$\ln(-c_{B}/s^{-1}) = -(67.0 \pm 14.1)\text{kJ mol}^{-1}/RT + (8.2 \pm 1.8)$$

(E9)

4. Discussion

We will start by considering whether there may be systematic errors interfering with the results reported. We will consider first various physical interferences, such as heat, momentum and mass transfer, and then various chemical processes, such as surface reactions and possible parallel processes. We will then consider the lessons to be drawn from these experiments, and compare the results with theoretical predictions and with the results of earlier experiments, where appropriate.

1 0 -2 -3 1.04 1.08 1.12 1.16 1000 K/T

Fig. 7 Arrhenius plots for the absolute values of the parameters, c, for secondary reactions; (\blacksquare) vinylacetylene; (\blacktriangle) benzene.

4.1. Effect of incomplete radial heat transfer

In a conventional flow reactor, it is often assumed that gas is instantly warmed to the reactor temperature. However, when gas flows through the reactor too fast, *i.e.* when the residence time of gas in the reactor is too short, an error may be introduced because of the delay in warming up the gas. The gas temperature on the axis at the inlet of the reactor would be lower than that near the wall. Mulcahy and Pethard⁴⁴ derived an equation,

$$k_{\rm app}/k = 1 - (r^2/(3.658\kappa t))[0.577 + \ln\{0.82E_{\rm A}(T_{\rm w} - T_{\rm i})/(RT_{\rm w}^2)\}]$$
(E10)

Here, k_{app} is the apparent first-order rate constant when radial heat transfer is incomplete; k, the true first-order rate constant; r, the radius of the reactor; κ , the coefficient of thermal diffusivity; t, the residence time; E_A , the activation energy; T_w , the temperature of the reactor wall; and T_i , the temperature of the entering reactant.

Thermal properties of acetylene were obtained from ref. 45. Using the activation energies and the reactor radii, residence times and temperatures from the present work, the maximum reduction in k_{app} because of incomplete radial heat transfer was calculated to be 4%. This may be compared to the experimental reductions in rates of between 60% and 80% observed in Fig. 1 and 2. We conclude that the induction periods observed were not caused by incomplete radial heat transfer.

4.2. Pressure drop, axial diffusion and volume contraction

The Reynolds number was estimated to be in the range between 0.20 and 24, so laminar flow was established in the present work. A gas flowing through a reactor can cause a pressure drop along the reactor, because there is friction between the reactor wall and the moving gas, especially at high flow rates. The magnitude of the pressure drop, which can be measured readily by measuring pressures at the entrance and the exit of a reactor, mainly depends on the temperature, the pressure, the flow rate, and the dimensions of the reactor. The pressure drop in the present work was minimized by using short reactors. Measured pressure drops were always less than 10%, so the effect of pressure drop was negligible.

It is generally assumed that all the gas molecules spend the same length of time in the reactor. Actually, the occurrence of the reaction causes a concentration gradient of the reactant in the reactor, which in turn causes axial diffusion of the reactant toward the exit. The residence time for the reactant would be shorter than the calculated value. On the other hand, the parabolic velocity profile in the reactor could cause radial diffusion of the reactant. Furue and Pacey⁴⁶ investigated the effect of mass transfer in the pyrolysis of cyclopropane in cylindrical flow reactors and found that the apparent first order rate constant was reduced by 10% only at conversions of 83% or more. Hence, the effect of mass transfer was not significant at the low conversions of less than 1.4% in the present work. The Peclet number was calculated to be between 4 and 1800, also indicating that diffusion was insignificant compared to convection.

When a reaction occurs in a reactor, the total number of moles of gas in the reactor may change. A decrease in the number of moles would result in a volume contraction. In this case, the molecules in the reactor would leave the reactor more slowly. Thus, the actual residence time of molecules in the reactor would be longer than the value calculated from the flow rate, pressure, and temperature in the reactor. The low conversions in this work should not have resulted in a significant volume contraction.

4.3. Surface reaction and the effect of impurities

A possible source of error is a surface reaction, which would vary in importance in reactors with different diameters. A

carbon deposit on the surface was found in previous work⁴² to inhibit the formation of gaseous products by a heterogeneous termination process. Washing the reactor with HF and burning off the carbon deposit almost eliminated this inhibition. These procedures were followed in the present work.

Eqn. (E1) applies to a mechanism with a bimolecular termination process. It has been shown elsewhere⁴⁷ that, if termination occurs by a unimolecular, surface process, the induction period is inversely proportional to k_t . If a surface reaction is limited by the first-order rate of reaction of radicals at the surface, the induction period will be independent of $[C_2H_2]$. If a surface reaction is limited by diffusion, the induction period will be proportional to the gas pressure. Neither of these hypotheses would predict the inverse proportionality between τ and [C₂H₂] observed in Fig. 3. We conclude that chain termination in the present system occurs in the gas phase. If the termination occurs by bimolecular removal of two intermediates, eqn. (E1) and (E2) in the Introduction are appropriate. If termination occurs by a collision between the key intermediate and acetylene, the induction period would be equal to $(k_1[C_2H_2])^{-1.47}$ This possibility also agrees with the observed order in Fig. 3, and will be considered further in the next two sections.

The results at the highest concentrations in Table 1 and Fig. 3 and 4 were obtained using reactors of different diameters. These results agreed very well with the trends established at lower concentrations in the large reactor.

The main impurity in acetylene was acetone, which is a source of free radicals at high temperatures. It was previously found that acetone had no significant effect on the pyrolysis of acetylene when its mole fraction was less than 400 ppm.⁴⁸ In the present work, its mole fraction was controlled to be less than 120 ppm. The rates of initiation reactions from acetone, propylene, propane and ethane impurities in the purified acetylene were estimated from the concentrations in Section 2 and from rate constants in the literature^{39,49–51} to be 5.9×10^{-9} , 4.7×10^{-16} , 1.4×10^{-9} and 2.3×10^{-11} mol L⁻¹ s⁻¹, respectively. The value for initiation by acetone was the largest of these, so initiation by propylene, propane and ethane should also be negligible.

4.4. Mechanism of the reaction

As mentioned in the Introduction, molecular mechanisms involving vinylidene and free radical mechanisms have both been proposed to interpret the pyrolysis of acetylene. The lifetime for vinylidene in a vacuum was determined to be $3.5 \,\mu\text{s}$ by Levin *et al.*⁴¹ A multiple barrier recrossing between vibrationally excited acetylene and vinylidene was simulated by Hayes *et al.* using *ab initio* molecular dynamics methods.⁵² At the gas pressures used in the present work, the lifetime of vinylidene would be determined by its deactivation by collision with other molecules. Assuming deactivation on every collision, the lifetime is estimated to be 1–5 ns in our system, seven orders of magnitude shorter than the induction periods observed.

The lifetime of the propargylmethylene intermediate, CH₂CCHCH, proposed by Kiefer and Von Drasek,²⁹ was estimated to be between 10^{-11} and 10^{-12} s at 854–970 K, using the rate constant for its conversion to vinylacetylene suggested by Benson.²¹

The contribution of a molecular mechanism should be independent of the residence times used in the present work. When a term, d, representing the contribution of a molecular mechanism is added into eqn. (E1), we obtain,

$$[P]/t = d + [(b_P/t)\ln\{[1 + \exp(a_P t)]/2\} - a_P b_P/2](1 - c_P t)$$
(E11)

Table 2 shows the ratio, d/R^{ss} , of the rate of a possible molecular process to the full steady-state rate, obtained by fitting eqn. (E11) to the data for vinylacetylene and for benzene. The uncertainties in the parameters *a*, *b* and *c*, increased by factors between 2 and 5. Uncertainties greater than 50% in most cases, and negative values in some cases, were obtained for the parameter, *d*. The average value of d_{VA}/R_{VA}^{ss} , expressed as a percentage, was $(2.6 \pm 7.7)\%$. Therefore, the contribution from a molecular mechanism to the formation of vinylacetylene (d_{VA}/R_{VA}^{ss}) was negligible. At 934–936 K, the maximum contributions from a molecular mechanism to the formation of benzene (d_B/R_B^{ss}) were about 30%. The average value of d_B/R_B^{ss} in the table was $(15 \pm 15)\%$. This leaves open the possibility of a minor, molecular pathway leading to the formation of benzene.

It is necessary to distinguish the present induction period from another period of time, the auto-acceleration period, which has sometimes been called an induction period in previous work. When significant amounts of products have been formed, one or more of these products could introduce new sources of free radicals. Therefore, the entire reaction could be accelerated. Auto-acceleration has been observed at higher conversions in the pyrolysis of acetylene by some previous workers. Frank-Kamenetzky53 found an auto-acceleration period of 12 s at 192 Torr and 877 K in a flow system. He found the auto-acceleration period was proportional to the inverse square of $[C_2H_2]$ at temperatures above 773 K. Minkoff et al.54 observed an auto-acceleration period of 48 s at 236 Torr and 773 K in a static reactor. Cullis and Franklin⁸ observed an auto-acceleration period between 10 and 20 s at pressures from 270 to 370 Torr over the temperature range 828-938 K. These auto-acceleration periods were two or three orders of magnitude longer than the induction periods observed in the present work, and represent a distinct chemical phenomenon. The rates at short residence times in Fig. 1 and 2 in the present work appeared to approach zero, whereas a finite rate was observed at short residence times in the previous studies. Auto-acceleration was observed for benzene in the present work. If the data at residence times less than 0.2 s were deleted from Fig. 2, we would have a similar situation to that reported by the earlier workers.8,53,54 The rate of benzene formation would increase with increasing residence time, but, without the first few data points, there would appear to be a finite initial rate. Benson²¹ interpreted auto-acceleration as the result of the build-up of vinylacetylene concentration in the system.

In the present work, both vinylacetylene and benzene were found to be primary products. The induction periods in Table 1 were between 35 and 150 ms. These are seven orders of magnitude slower than the relaxation time for vinylidene, and nine orders of magnitude slower than the lifetime for propargylmethylene. They are one or two orders of magnitude slower than radial heat transfer. They are two or three orders of magnitude faster than auto-acceleration.^{8,53,54} They are

Table 2 Estimated fractional rates of formation of vinylacetylene and benzene from a possible, parallel, molecular pathway obtained by nonlinear least-squares fits of eqn. (E11) to the experimental data^{*a*}

T/\mathbf{K}	P/ Torr	$d_{ m VA}/R_{ m VA}^{ m ss}$	$d_{ m B}/R_{ m B}^{ m ss}$
970	53	0.059 ± 0.082	0.18 ± 0.09
970	36	0.070 ± 0.071	0.10 ± 0.02
936	69	0.13 ± 0.07	0.30 ± 0.08
934	34	-0.087 ± 0.006	0.27 ± 0.05
935	27	-0.0008 ± 0.0312	-0.019 ± 0.004
895	60	0.066 ± 0.116	-0.072 ± 0.126
854	120	-0.053 ± 0.181	0.30 ± 0.48

^a Non-linear least-squares fits did not converge at 938 K and 126 Torr, and at 934 K and 52 Torr.

similar to the induction periods caused by the establishment of free radical concentrations in other pyrolysis systems.^{35–39} This is crucial evidence for a free radical mechanism in the pyrolysis of acetylene. Molecular mechanisms involving vinylidene^{24,29} do not appear to play a dominant role in the present work. However, we cannot rule out a minor contribution from a molecular mechanism to the formation of benzene.

The similarity of the induction periods for vinylacetylene and for benzene indicates that both vinylacetylene and benzene were formed from the same free radicals or from free radicals which could rapidly interconvert.

4.5. Properties of the initiation and termination reactions

The order of the initiation reaction may be estimated using eqn. (E2). It is twice the absolute value of the slope of a graph of $\log_{10} \tau vs. \log_{10}[C_2H_2]$, as shown in Fig. 3. The order of the initiation reaction can be calculated to be 2.18 ± 0.14 from the vinylacetylene data, 2.4 ± 0.6 from the benzene data, and 2.2 ± 0.2 from the data for both vinylacetylene and benzene. A second-order initiation reaction was supported.

Most radical recombination reactions have rates which are almost independent of temperature. Sometimes there is a dependence on $T^{1/2}$ or $T^{-1/2}$, corresponding to an activation energy of $\pm 0.5 \ RT$, or $\pm 4 \ kJ \ mol^{-1}$ at the temperatures of this work. Therefore, the temperature dependence of the product, $k_i k_t$, in eqn. (E3) to (E5) must be almost entirely associated with k_i . The activation energy for the initiation reaction may be derived to be $268 \pm 12 \ kJ \ mol^{-1}$ from the data for vinylacetylene, $231 \pm 38 \ kJ \ mol^{-1}$ from the data for benzene and $261 \pm 11 \ kJ \ mol^{-1}$ from the combined data.

The singlet-triplet gap for acetylene was experimentally determined to be 346 kJ mol^{-1,⁵⁵} which is much higher than the activation energy for initiation in the present paper. Therefore, Minkoff's triplet-initiation mechanism can be ruled out.

Back's initiation reaction,¹⁸

$$2C_2H_2 \rightarrow C_2H + C_2H_3 \tag{1}$$

can be ruled out, because its activation energy was calculated using *ab initio methods*²⁴ to be 370 kJ mol⁻¹, which is again much higher than the activation energy determined in the present work.

Unimolecular initiation by the rupture of a C-H bond in acetylene,

$$C_2H_2 + M \rightarrow C_2H + H + M \tag{2}$$

was important at much higher temperatures. The activation energy for this reaction was calculated to be 508 kJ mol⁻¹ at 1000 K, using recent experimental results reported by Kruse and Roth¹⁷ at 2580 to 4650 K. This energy is almost twice as great as our activation energy, so unimolecular initiation was not important in this work.

The rate constant for an initiation reaction involving the formation of C_4H_3 and H,

$$2C_2H_2 \rightarrow C_4H_4^* \rightarrow C_4H_3 + H \tag{3}$$

has been estimated by some previous workers using thermochemical methods. Tanzawa and Gardiner¹⁹ suggested a rate constant of 2×10^9 L mol⁻¹ s⁻¹ exp(-192 kJ mol⁻¹/RT). Wu and co-workers¹⁵ estimated an expression of 2×10^{10} L mol⁻¹ s⁻¹ exp(-186 kJ mol⁻¹/RT). Kiefer *et al.*¹⁶ predicted an expression of 1.5×10^{11} L mol⁻¹ s⁻¹ exp(-234 kJ mol⁻¹/ *RT*). Melius *et al.*⁵⁶ calculated an activation energy of 231 ± 15 kJ mol⁻¹ for this reaction by *ab initio* methods. The values estimated by Kiefer *et al.* and by Melius *et al.* are very close to the value determined from the benzene data in this work. The lowest energy form of C₄H₃ plus H was calculated to be 179.7 kJ mol⁻¹ more stable than C(³P) plus allene using *ab initio* MO methods.⁵⁷ Combining this result with the enthalpies of formation of the latter species and of acetylene, the activation energy for reaction (3) could be calculated to be 273 kJ mol⁻¹. This value is very close to that determined from the data for vinylacetylene in the present work.

The rate constant of this initiation reaction has also been measured experimentally. One of the possible products of the initiation reaction, C₄H₃, was observed in a shock tube at 1600-2400 K by Gay et al.¹⁰ They assumed that the rate of the initiation reaction was equal to the rate of formation of diacetylene, for which an induction period was observed in their system. The Arrhenius expression for initiation was calculated to be 2.95×10^{10} L mol⁻¹ s⁻¹ exp(-162 kJ mol⁻¹/ RT). Frank and Just¹³ observed another possible product of the initiation reaction, H, in a shock tube at 1850-3000 K. The concentration of H built up to a steady-state value following an induction period. They first assumed that the only source of H atoms was reaction (2), but the Arrhenius curve for this reaction was found to bend up at their lowest temperatures, 1850-2000 K, indicating that there was an additional source of H atoms, which was suggested to be reaction (3). However, they did not propose an Arrhenius expression for this initiation reaction because of the narrow range of temperatures. They found that their rate constant was 12 times slower than that reported by Gay et al.,¹⁰ and suggested that a chain reaction might have been involved in the earlier experiments.

Dimitrijevic *et al.*⁴⁸ obtained an Arrhenius expression of $10^{12.7\pm0.9}$ L mol⁻¹ s⁻¹ exp(-253 ± 15 kJ mol⁻¹/*RT*) for a bimolecular, initiation reaction, assuming a first-order, surface termination, by studying the acceleration of the pyrolysis of acetylene by acetone at 914–1039 K.

A C_4H_4 triplet, H_2 CCCC H_2 , was calculated using *ab* initio MO methods⁵⁷ to be 224.7 kJ mol⁻¹ more stable than C_4H_3 plus H. Using the *ab* initio enthalpy of C_4H_3 above,⁵⁶ the enthalpy change for the formation of C_4H_4 triplet from acetylene would be only 6 ± 15 kJ mol⁻¹. The original authors⁵⁷ did not suggest this triplet would participate in acetylene pyrolysis, but it is energetically accessible, so it must be considered further.

If the triplet, C_4H_4 , was the main chain carrier, net removal of the triplet species could occur by three possible pathways, *i.e.* unimolecular intersystem crossing to a singlet, bimolecular quenching to a singlet, or bimolecular triplet-triplet annihilation. The first, unimolecular process would lead to an induction period independent of $[C_2H_2]$, contrary to the experimental observations. Bimolecular quenching and triplet-triplet annihilation would agree with the observed concentration dependence.

In the case of bimolecular quenching between a triplet and an acetylene molecule, the expression for the induction period could be derived as,

$$\tau = 1/(k_q[C_2H_2])$$
 (E12)

Here, k_a is the rate constant of bimolecular quenching. To agree with the experiments, this quenching process would need to have a pre-exponential factor equal to the square root of $10^{23.1\pm0.4}$ L² mol⁻² s⁻², *i.e.* 3.6×10^{11} L mol⁻¹ s⁻¹, and an activation energy of 130 ± 4 kJ mol⁻¹. The Arrhenius parameters for k_q could be estimated from the parameters for similar processes. The pre-exponential factor and the activation energy for the quenching of triplet acetophenone by singlet acetophenone were reported to be 2.5×10^8 L mol⁻¹ s⁻¹ and 1.3 kJ mol⁻¹ in the gas phase, and 6.3×10^6 L mol⁻¹ s⁻¹ and 2.1 kJ mol⁻¹ in solution, respectively.⁵⁹ Typical preexponential factors for quenching of various triplet species in solution were determined to lie between 10^6 and 10^{10} L mol⁻¹ s⁻¹.⁶⁰ We can find no precedent for an activation energy for quenching as high as $\hat{1}30 \text{ kJ mol}^{-1}$, nor for a preexponential factor as high as 3.6×10^{11} L mol⁻¹ s⁻¹ for this spin-forbidden process. Therefore, we can rule out bimolecular

quenching of a triplet as the process responsible for the observed induction periods.

In the case of triplet-triplet annihilation, by analogy with eqn. (E1) an expression for the induction period could be derived, as follows:

$$\tau = 1/(k_{\rm SS} k_{\rm TT} [C_2 H_2]^2)^{0.5}$$
(E13)

Here, $k_{\rm ss}$ is the rate constant for the formation of C_4H_4 triplet from two singlet acetylene molecules, and $k_{\rm TT}$ is the rate constant for the triplet-triplet annihilation. To agree with the constant term in eqn. (E5), these processes would need to have the product of their pre-exponential factors equal to $10^{23.1\pm0.4}$ L² mol⁻² s⁻². The pre-exponential factor for the bimolecular interaction of singlet methylene and singlet acetylene to form triplet methylene and singlet acetylene in the gas phase was reported to be 4.8×10^{10} L mol⁻¹ s⁻¹.⁶¹ The preexponential factor for the bimolecular removal of two triplet methylenes in the gas phase was reported to be 1.2×10^{10} L mol⁻¹ s⁻¹.⁶¹ The product of these two numbers is 5.8×10^{20} L² mol⁻² s⁻², more than two orders of magnitude slower than the value determined in the present work. Slow preexponential factors from 10^8 to 10^{10} L mol⁻¹ s⁻¹ were also found for deactivation of large organic triplets by triplet oxygen in solution.⁶⁰

Furthermore, the deactivation of C_4H_4 triplet, H_2 CCCC'H₂, should produce butatriene, which was not observed experimentally. *Ab initio* calculation showed that butatriene was only 26.7 kJ mol⁻¹ less stable than vinylacetylene, and that there was a high barrier, 320 kJ mol⁻¹, for the conversion of butatriene to vinylacetylene.⁵⁶ The conversion from butatriene to vinylacetylene should not be significant in the present work. Therefore, no significant amount of C_4H_4 triplet, H_2 CCCC'H₂, could have been formed in the present work.

In view of the foregoing, the only initiation reaction which is consistent with the order, activation energy and product distribution observed in the present work is reaction (3). Recent workers⁵⁶ suggest this reaction occurs by the isomerization of an acetylene molecule to vinylidene, which adds to another acetylene to give a vibrationally excited, singlet C₄H₄ complex, which decomposes to C₄H₃ and H. These two radicals would then add to acetylene, producing further radicals which would participate in the main chain reaction.

The constant term in eqn. (E5) corresponds to a product of the pre-exponential factors, A_iA_t , for initiation and termination of $10^{23.1\pm0.4}$ L² mol⁻² s⁻². Vinylidene, with three rotational degrees of freedom, would be expected to have a higher entropy than acetylene, which has only two rotational degrees of freedom. Provided the attack of vinylidene on acetylene and the radical recombination occur with pre-exponential factors near the collision limit, the magnitude of the product, A_iA_t , above can be explained.

4.6. Properties of the steady-state rates

The order for the formation of vinylacetylene was determined by some previous workers; results are summarized in Table 3. Ogura¹² found an order of 2.35 while most other workers reported an order of two. When vinylacetylene was the main View Article Online product, the order for the decomposition of acetylene would approximately equal the order for the formation of vinylacetylene. The order for the decomposition of acetylene was measured by many previous workers, and the results were reviewed by Colket *et al.*²⁰ Most orders were found to be between 1.5 and 2.0. Most workers favored an order of two.

The second-order rate constant for the formation of vinylacetylene has been measured by several groups. Arrhenius parameters are also summarized in Table 3. The large variations in these parameters may be caused by the presence of auto-acceleration in experiments at higher conversions and by the presence of surface reactions in earlier work in static and flow reactors. In shock tube studies, the dominant initiation reaction may be reaction (2). The absolute rate constants are compared in Fig. 8. The rate constants from the present work lie between the results of Dimitrijevic *et al.*⁴⁸ and those of Duran *et al.*⁶² It should be pointed out that the rate constant determined in the present work may have a small systematic error, because but-1-ene was used to calibrate the GC peaks for vinylacetylene.

Benzene was also found to be a primary product in the pyrolysis of acetylene at 1273 K by Becker and Huttinger.⁶³ The order for the formation of benzene was suggested to be a combination of first and third order, depending on the residence time. The rate of formation of benzene could be calculated from their results to be 8.60×10^{-5} mol L⁻¹ s⁻¹ at 60 Torr and 1273 K. This is five times faster than the value calculated using our eqn. (E7). The third-order rate constant for the formation of benzene was reported to be $10^{11.6\pm0.9}$ L² mol⁻² s⁻¹ exp(-164 ± 17 kJ mol⁻¹/*RT*) by Dimitrijevic *et al.*⁴⁸

In the present work, expression (E7) has an order of 2.4, instead of an integer. There are various interpretations of the fractional factor. One explanation could be that benzene was formed by two parallel pathways with different orders. Different free radicals might have been involved. Therefore, the order observed would be a combination of the two orders of the pathways. According to the polymerization mechanism



Fig. 8 Arrhenius plot for $k_{VA}/L \mod^{-1} s^{-1}$; (\bullet) Bradley and Kistiakowsky;⁷⁰ (\blacktriangle) Ogura;¹² (\bigstar) Kiefer *et al.*;⁷¹ (\blacktriangledown) Duran *et al.*;⁶² (\blacklozenge) Dimitrijevic *et al.*;⁴⁸ (\Box) this work.

 Table 3
 Orders and Arrhenius parameters measured for the formation of vinylacetylene

Ref.	Apparatus	T/K	$\log(A/L^{n-1} mol^{1-n} s^{-1})$	$E_{\rm A}/{\rm kJ}~{\rm mol}^{-1}$	Order
70	shock tube	1800-2700	11.56	185	2
12	shock tube	1000-1670	13.74 ± 1.05	201 ± 6	2.35 ± 0.15
71	shock tube	1700-2400	10.77	187	2 –
62	static reactor	770-980	9.74 + 0.20	155	2
48	flow reactor	914-1039	11.8 + 0.7	208 + 13	2
This work	flow reactor	854-970	9.86 ± 0.65	165 ± 11	1.8 ± 0.1

suggested by Benson,²¹ a series of free radicals of different lengths could be formed. A second explanation could be that benzene was limited by different, consecutive steps in a mechanism, *e.g.*, the rate-determining step for the formation of benzene could be

$$C_2H_2 + C_2H_3 \rightarrow C_4H_5 \tag{4}$$

at high pressures and

$$C_2H_2 + C_4H_5 \rightarrow C_6H_7 \tag{5}$$

at low pressures. The combination of these two cases would lead to an order between 2 and 3. A third possibility is that two or more free radicals might be involved in termination reactions, which would also lead to a fractional order.

4.7. The parameters, *b*

Using eqn. (E2) and the definitions following eqn. (E1), it may be readily shown that the parameter b equals $R^{ss}\tau/2$. This parameter may be obtained by multiplying the parameters listed in the fourth and sixth columns of Table 1. An expression for $\ln(b/[C_2H_2])_{VA}$ can be derived from eqn. (E3) and (E6) as,

$$\ln(b/[C_2H_2])_{VA} = -(31 \pm 12)kJ \text{ mol}^{-1}/RT - (5.0 \pm 1.6)$$
(E14)

Now we know that both the initiation and termination reactions are bimolecular, it is possible to obtain an expression for the steady-state concentration of the radical, X, removed in the termination step.

$$[X]_{ss} = (k_i [C_2 H_2]^2 / k_t)^{1/2}$$
(E15)

The case where there is more than one termination step has been considered by Come.⁶⁴ [X]_{ss} depends on the first power of [C₂H₂], whereas R_{VA}^{ss} has been shown to be approximately proportional to [C₂H₂]². So R_{VA}^{ss} can be related to [X]_{ss} as follows:

$$R_{\rm VA}^{\rm ss} = k_{\rm p}[{\rm X}]_{\rm ss}[{\rm C}_2{\rm H}_2] \tag{E16}$$

Here, k_p is an effective rate constant for propagation. It may be that X does not lead to vinylacetylene in one step but by several steps involving the rapid interconversion of radicals. Combining eqn. (E2), (E15) and (E16), we find the quotient in eqn. (E14) is related to k_p and k_t .

$$b_{\rm VA}/[\rm C_2H_2] = k_p/(2k_t)$$
 (E17)

Again the termination rate constant, k_t , is likely to have only a weak temperature dependence, so the activation energy, $31 \pm 12 \text{ kJ mol}^{-1}$, in eqn. (E14) must be similar to the activation energy for k_p . The constant term, -5.0 ± 1.6 , indicates that k_p has a pre-exponential factor lower than that for k_t by about two orders of magnitude.

The activation energy for reaction (4) has been estimated to be 25 kJ mol⁻¹ using a thermochemical method⁶⁵ and 36 kJ mol⁻¹ from an *ab initio* calculation.⁶⁶ These values are within the range of uncertainties in eqn. (E14).

Because of the greater uncertainties in the benzene data, it is not possible to perform a similar analysis.

4.8. The parameters, c

Auto-acceleration was observed in the formation of benzene in the present timescale. (The parameter $c_{\rm B}$ was always positive.) This process might involve secondary reactions of vinylacetylene with free radicals. The amounts of vinylacetylene removed and of benzene formed by secondary reactions can be compared by examining the products $b_{\rm VA} c_{\rm VA}$ and $-b_{\rm B} c_{\rm B}$. The fact that $b_{\rm VA} c_{\rm VA}$ values were two to seven times larger than $b_{\rm B} c_{\rm B}$ values indicates that vinylacetylene might have been involved in several secondary reactions, including its conversion to benzene and the continuous addition of C_2 units to form C_8 and higher species.

Vinylacetylene was reported to be a reactive species at high temperatures.⁶⁷ The first-order rate constant for the total removal of vinylacetylene in the pyrolysis of pure vinylacetylene in a shock tube⁶⁸ was reported to be $6.1 \times 10^{13} \text{ s}^{-1} \exp(-334 \text{ kJ mol}^{-1}/RT)$. This is about four orders of magnitude smaller than the value of c_{VA} from eqn. (E8) at 970 K in the present work. The activation energy reported was three times greater than the value measured in the present work. This indicates that the main secondary reaction of vinylacetylene in the present work was not the unimolecular decomposition of vinylacetylene.

The rate of vinylacetylene removal in the pyrolysis of an equimolar mixture of acetylene and vinylacetylene in a static vessel at 723 K⁶⁹ was shown to be 2.6×10^{-6} mol L⁻¹ s⁻¹. This rate is about half the value calculated using eqn. (E8). This agreement within a factor of two indicates that the main secondary reaction of vinylacetylene in the present work is a bimolecular reaction between vinylacetylene and a radical whose concentration is almost independent of the pressure of acetylene. According to eqn. (E15) this radical is not the main, chain-terminating radical. The radical removing vinylacetylene is probably a smaller radical, such as a hydrogen atom.

5. Conclusion

Induction periods for the formation of vinylacetylene and benzene have been observed between 854 and 970 K. This is the first observation of an induction period, distinct from an auto-acceleration period, in acetylene pyrolysis below 1600 K. This is crucial evidence for a free radical mechanism. Any contribution from a parallel, molecular mechanism was too small to be reliably established. The initiation reaction was shown to involve two acetylene molecules. The termination reaction is a bimolecular, gas phase, radical combination. The product of the rate constants for the initiation and termination steps was determined from the induction periods. The initiation reaction was shown to have an activation energy of approximately 260 kJ mol⁻¹. The orders and the rate constants for the formation of vinylacetylene and benzene were determined. Vinylacetylene was formed from a reaction or series of reactions involving the main, chain-terminating radical, X, and an additional molecule of acetylene. These reactions have an overall activation energy of 31 ± 12 kJ mol⁻¹. Benzene has an overall order of formation of 2.4. Its overall activation energy of formation is only $100 \pm 9 \text{ kJ mol}^{-1}$, indicating it is formed from intermediates with a lower enthalpy than the main, chain-terminating radical.

To obtain more information regarding the mechanism of the pyrolysis of acetylene, more experiments will be performed to study the rate constant for the initiation reaction by investigating the acceleration of the reaction by additives, and to search for products heavier than benzene.

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