

Unimolecular Dissociation of Vinylacetylene: A Molecular Reaction

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The thermal decomposition of vinylacetylene (C_4H_4) has been studied in the shock tube with two time-resolved diagnostics, laser-schlieren (2% and 4% C_4H_4 -Kr, 1650–2500 K, 110–427 Torr) and time-of-flight mass spectrometry (2% C_4H_4 -Ne, 1500–2000 K, 150–300 Torr). The time-of-flight mass spectra show dominant products C_2H_2 and C_4H_2 with a very consistent 5:1 ratio of C_2H_2 to C_4H_2 , in essential agreement with earlier shock tube results. The laser-schlieren semilog density gradient profiles are all concave-upward, showing no trace of chain acceleration. Analysis of these profiles also sets the effective heat of reaction between 30 and 50 kcal/mol. Rate constants calculated from the zero-time gradients assuming $\Delta H^\circ_{298} = 40$ kcal/mol are fit with a routine RRKM model which indicates a barrier $E_0 = 79.5 \pm 3$ kcal/mol. These observations and the time-of-flight product profiles are consistent with the molecular reactions $C_4H_4 \rightarrow 2C_2H_2$ ($\Delta H^\circ_{298} = 39$ kcal/mol) and $C_4H_4 \rightarrow C_4H_2 + H_2$ ($\Delta H^\circ_{298} = 42$ kcal/mol). Detailed balance rate constants for $2C_2H_2 \rightarrow C_4H_4$ are in good agreement with the extensive previous data on the second-order acetylene reaction, confirming that vinylacetylene is a direct and dominant product of C_2H_2 dimerization for moderate temperatures. Above 1500 K, the C_4H_4 dissociation shows significant falloff even for high pressures, and the now dominant C_4H_2 in C_2H_2 pyrolysis may then be formed in part through $2C_2H_2 \rightarrow C_4H_2 + H_2$. It is proposed that vinylacetylene dissociates as a substituted ethylene, either by 1,1-elimination of molecular hydrogen, leaving vinylidene acetylene which rapidly isomerizes to C_4H_2 , or by 2,2-elimination of C_2H_2 , followed by rapid isomerization of the vinylidene to a second C_2H_2 . This mechanism is consistent with the observed barrier, provides a rationale for the constancy of the C_2H_2/C_4H_2 ratio, and offers a reasonable explanation for the magnitude (A factor) of the observed rate constants.

Introduction

Vinylacetylene (C_4H_4 , 1-buten-3-yne, VA) is both a common product of hydrocarbon pyrolysis and oxidation and an important intermediate of high stability on the path of dehydrogenation to acetylene and soot.¹ It is also a major product of acetylene pyrolysis; in fact, it may well be the sole initial product.²⁻⁶

Pyrolysis of VA for low to moderate temperatures (<1000 K)⁶⁻¹⁰ is primarily a polymerization with a few volatile products such as various C_8H_8 , benzene, and acetylene. At higher temperatures hydrogen, diacetylene, and methane appear, the latter probably arising from polymer carbonization or heterogeneous reaction.

Until quite recently there had been only one very limited look at the unimolecular dissociation of VA.¹¹ Like benzene, ethylene, and acetylene, this molecule has only very strong C–C bonds (the central single bond evidently has $D_0 > 130$ kcal/mol^{12,13}) and will not dissociate easily. Thus, it has taken the shock tube, with its unlimited temperature capability and assured homogeneity, to see the unimolecular process.

Colket¹⁴ has used the single-pulse shock tube technique to define product distributions from both very dilute (100 ppm) and relatively concentrated (1%) mixtures of VA in argon. These ex-

periments employed heating times of 700 μ s, pressures of 8 atm, and temperatures of 1100–2400 K. The major products are C_2H_2 and C_4H_2 with a very consistent 7–10:1 ratio of C_2H_2 to C_4H_2 . Lesser products, about an order of magnitude below C_4H_2 , and mainly discerned in the 1% mixture, include C_6H_6 , C_8H_6 (phenylacetylene), C_8H_8 , $C_{10}H_8$, and the higher polyacetylenes C_6H_2 and C_8H_2 . Hidaka et al.¹⁵ observed the variation of C_4H_4 absorption at 230 nm in incident shock waves using 0.5% and 0.75% C_4H_4 in Ar for 0.3–0.6 atm and 1200–1750 K. They additionally report a product analysis over 1400–1500 K which confirms the near 10:1 ratio of C_2H_2 to C_4H_2 reported by Colket.

Both of the above papers suggest VA decomposition is a chain reaction, with initiation by



which they take to be the sole dissociation channel. Rate constant expressions proposed for this dissociation were the following: Colket,¹⁴ $\log k_1$ (s^{-1}) = $15.2 - 85/\theta$ with $\theta = 2.303RT$ in kcal/mol; Hidaka et al.,¹⁵ $\log k_1$ (s^{-1}) = $13.8 - 80/\theta$ (1500–1700 K). Colket does not give a temperature range for his expression, but over 1500–1700 K his result is about a factor of 5 larger. Since Colket's pressures are still greater, this might indicate a strong unimolecular falloff. However, Hidaka et al. claim there is no indication of pressure dependence in their measured rates, even suggesting their rate constants should lie close to the high-pressure limit. Yet, as was noted by Colket, without serious falloff it is also difficult to understand such low activation energies for reaction 1.

In view of the restricted range of available measurements of VA dissociation, and the few cited inconsistencies, we have performed a fairly extensive series of new experiments on VA pyrolysis using both laser-schlieren (LS) and time-of-flight mass spectrometric (TOF) measurements on shock-heated VA–rare gas mixtures. The LS measurements afford a precise determination of initial dissociation rate free from interference by secondary reactions, as well as important kinetic information on major secondary paths. The TOF technique provides time-resolved concentration profiles for both reactant and major products. When combined with previous data, these methods are able to define

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TABLE I: Thermodynamic Data for Vinylacetylene^a

<i>T</i> , K	$(H^\circ - H^\circ_{298})/RT$	$-(F^\circ - H^\circ_{298})/RT$
600	5.694	35.58
800	7.864	37.53
1000	9.490	39.46
1200	10.778	41.31
1500	12.288	43.89
1800	13.452	46.24
2100	14.375	48.38
2300	14.890	49.72
2500	15.342	50.97
2700	15.742	52.17
3000	16.260	53.86

^a $\Delta H_f^\circ = 69$ kcal/mol.

the rate and products of the dominant channels in the unimolecular dissociation of vinylacetylene.

Experimental Section

The apparatus and procedures used in the LS experiments were as previously described.^{16,17} For these experiments VA was obtained from Wiley Organics, supplied in a steel container and stated to contain 3% xylene and a trace of *p*-*tert*-butylcatechol added as stabilizers. An initial mass spectral analysis of vapor showed serious contamination with CO₂, apparently inadvertently introduced during transfer over dry ice. A simple purification was thus carried out to remove both CO₂ and stabilizers.

Vapor from the cylinder was condensed in vacuo over dry ice-acetone, forming a clear, colorless liquid. Noncondensibles were removed and the liquid sample was warmed until about a third had vaporized, and this vapor was also discarded. A small subsequent fraction was then retained and mixed with Kr (Spectra Gases UHP) to form mixtures of 2% and 4% VA. Mass spectral analysis of the retained vapor fraction showed $96 \pm 3\%$ C₄H₄ with the remainder almost entirely C₂H₂ and H₂. These two are unlikely to have survived the purification procedure and are probably from some uncompensated cracking of the VA.

The experimental procedures and apparatus used for the TOF experiments on VA pyrolysis have largely been described elsewhere.^{18,19} Mass spectra taken at 30- μ s intervals were displayed on the screens of four oscilloscopes which were triggered in series. The mass spectral range covered *m/e* 10–100 up to a total observation time of 750 μ s. The peaks for various species that appeared were identified and their heights measured with an optical microscope. Ratios of reactive species peak heights to the inert gas (Ne or Ar) peak heights were then plotted as a function of time. The conversion to concentration profiles was accomplished with the aid of calibration plots constructed from measurements of peak height ratios obtained under no-reaction (low-temperature) shock conditions from a series of runs involving known concentrations of VA. The VA cracking pattern and its mass spectral sensitivity were derived from a series of mass spectra taken from runs performed under both low- and high-temperature shock conditions. The major cracking component observed from the C₄H₄ spectrum is C₄H₃ (*m/e* C₄H₃/C₄H₄ = 0.75).

For the TOF shock experiments VA was obtained from Wiley Organics as a 50% solution by weight in xylene. The cooled sample tube was attached to a glass vacuum system, and the VA purified by repeated bulb-to-bulb distillations. After the first and last fractions were discarded, a mixture of 2% VA in 99:1 Ne–Ar (liquid Carbonic research grade) was prepared.

The above mixture was now analyzed with the TOF, showing 0.12% xylene but no other impurities above 250 ppm. A mixture of 3% C₂H₂ in 99:1 Ne–Ar was also prepared and used for calibration. For temperatures below 1800 K, He was used as driver gas and higher temperatures used H₂. All experiments were

TABLE II: Initial and Frozen Reaction Conditions for the LS Experiments

shock no.	<i>P</i> ₁ , Torr	<i>U</i> ₁ , mm/ μ s	<i>P</i> ₂ , Torr	<i>T</i> ₂ , K
2.0% C ₄ H ₄ -Kr				
1	19.68	0.919	427	1717
2	18.02	0.942	411	1788
3	16.52	0.976	404	1896
4	15.54	0.997	396	1966
5	14.43	1.012	380	2017
6	15.02	1.015	399	2029
7	13.49	1.022	362	2053
8	13.95	1.030	381	2080
9	12.71	1.052	362	2155
10	11.28	1.081	342	2260
11	10.49	1.090	322	2292
12	9.93	1.110	317	2366
13	8.82	1.137	296	2469
14	8.05	1.561	279	2541
15	5.94	1.007	156	2003
16	5.11	1.011	135	2014
17	5.31	1.050	152	2149
18	4.85	1.070	144	2222
19	4.45	1.083	135	2267
20	4.06	1.101	128	2332
21	4.41	1.103	139	2340
22	3.69	1.153	125	2528
4.0% C ₄ H ₄ -Kr				
23	17.10	0.944	404	1671
24	16.04	0.954	387	1699
25	14.66	0.976	370	1765
26	14.99	0.977	380	1767
27	13.68	1.010	371	1866
28	13.05	1.022	363	1903
29	12.88	1.026	360	1913
30	11.98	1.030	338	1927
31	12.21	1.037	349	1949
32	11.56	1.040	332	1958
33	12.76	1.054	378	2004
34	10.75	1.055	319	2006
35	11.00	1.059	328	2018
36	10.23	1.075	315	2070
37	10.02	1.095	320	2134
38	9.70	1.100	312	2150
39	9.35	1.119	312	2215
40	4.54	1.037	129	1949
41	3.63	1.108	118	2177
42	3.24	1.141	112	2287

performed with loading pressures of 5.6 Torr and used an ionizing energy of 32 eV.

Calculations

Thermodynamic properties for VA were calculated from the rotational constants and frequencies given by Tørneng et al.²⁰ and are given in Table I. The heat of formation of VA was estimated as $\Delta H_f^\circ = 69$ kcal/mol, using the group additivity parameters of Benson.²¹ Frozen reaction conditions for all the LS experiments, as calculated from these thermodynamic data and the measured velocities, are presented in Table II. For these experiments estimated velocity errors correspond to a frozen temperature uncertainty of ± 5 K.

The time origin for reaction in the LS experiments was initially set as before²² and then delayed 0.2 μ s as now suggested by recent LS measurements on cyclohexene dissociation.²³

The properties of C₂H₂ and H₂ were those of the JANAF tables,²⁴ and the properties for C₄H₂ were those derived earlier,²⁵

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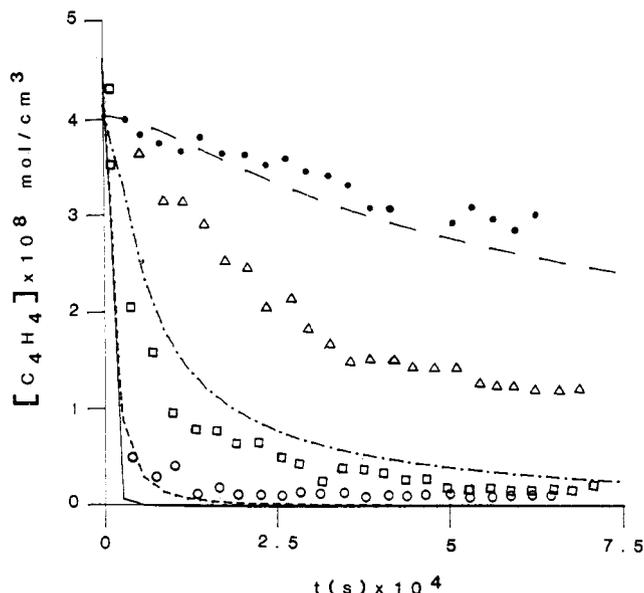


Figure 1. Profiles of VA (C_4H_4) concentration (relative to initial Ne concentration) from four TOF experiments in 2% C_4H_4 -Ne, with reflected shock frozen temperatures (in K): (●) 1492, (▲) 1688, (□) 1877, and (○) 2035. Postshock pressures are between 0.2 and 0.4 atm. The lines show the result of a modeling with the chain mechanism proposed by Colket¹⁴ at (---) 1492, (---) 1688, (---) 1877, (—) 2035 K.

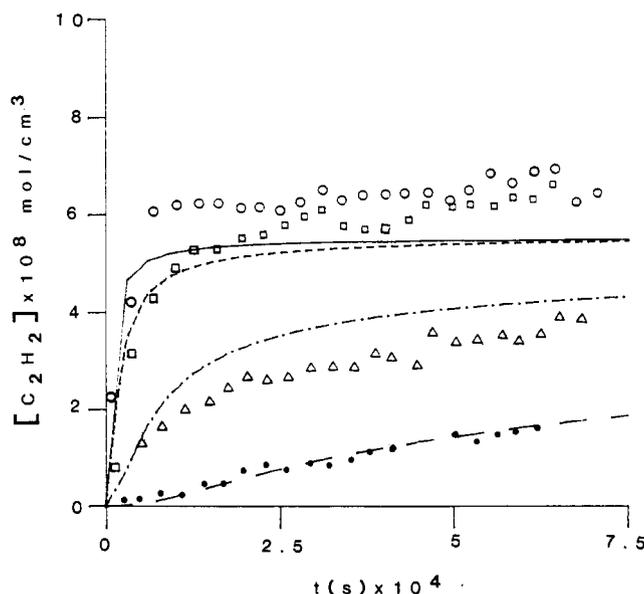


Figure 2. Profiles of C_2H_2 concentration (relative to initial Ne) from the four TOF experiments of Figure 1. The data and calculations are as in Figure 1.

using a $\Delta H_f^\circ_{298}(C_4H_2) = 112 \text{ kcal/mol}$.²⁶ In calculations using the chain mechanism for VA pyrolysis given by Colket,¹⁴ the heats of formation of radicals were those he suggested. Molar reactivities were 18.959 for VA and 6.367 for Kr.

The shock kinetics integration routines used herein have been described.^{19,27} The RRKM calculations use the direct vibrational state count with classical rotation program also previously described.²³

Results

TOF observations of species formation in the VA pyrolysis showed acetylene and diacetylene as major products with traces

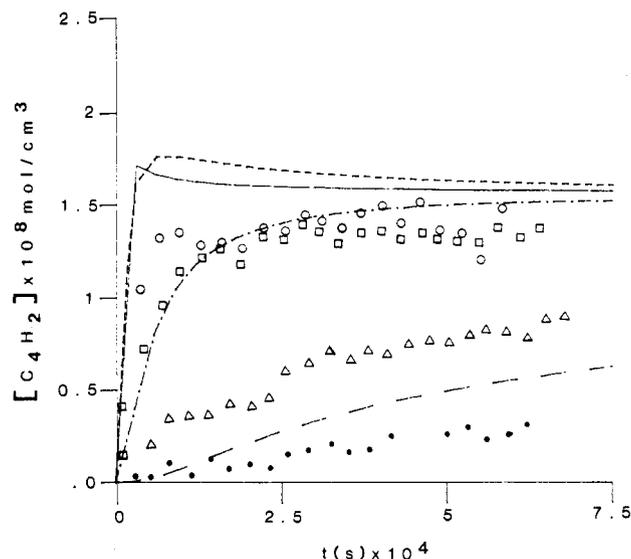


Figure 3. Profiles of C_4H_2 concentration (relative to initial Ne) from the four TOF experiments of Figure 1. The data and calculations are as in Figure 1.

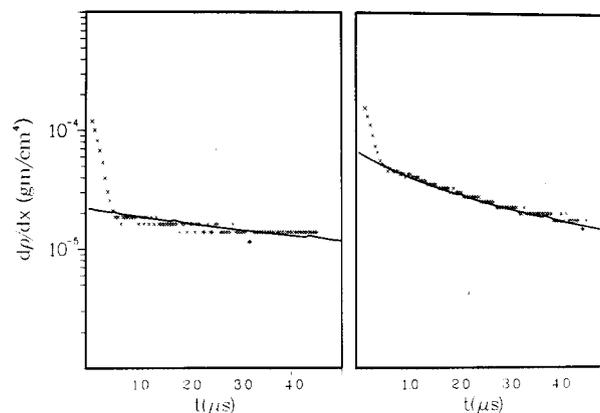


Figure 4. LS semilog density gradient profiles for two experiments in 4.0% VA-Kr, with frozen conditions 1768 K, 380 Torr and 1950 K, 350 Torr. The measured gradients are indicated by \times , and the solid lines show the result of simulations using an "optimum" rate for reaction 12 alone. The first few rapidly falling points, $t < 0.5 \mu\text{s}$, are affected by beam-shock front interaction.

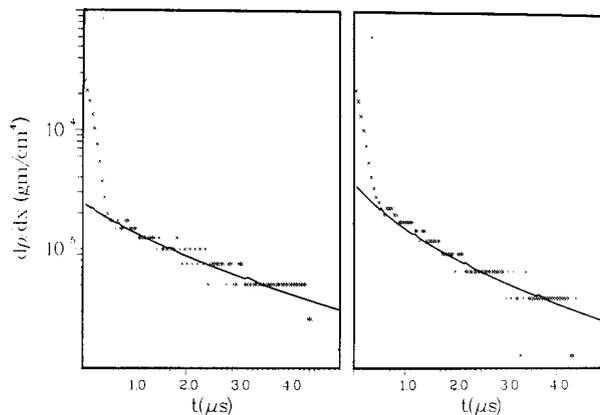


Figure 5. LS semilog density gradient profiles for two experiments at "low" pressures: 2% VA-Kr, 2149 K, 152 Torr; 4% VA-Kr, 2287 K, 113 Torr. Data are indicated by \times , and the calculations are as in Figure 4.

of C_6H_2 at the higher temperatures. No C_4H_3 , above that expected from cracking of the VA, could be detected. Profiles of unreacted VA and of product C_2H_2 and C_4H_2 are given in Figures 1–3. The ratio C_2H_2/C_4H_2 is seen to be near 5:1 for all temperatures and at all times, in essential agreement with Colket¹⁴ and Hidaka et al.¹⁵

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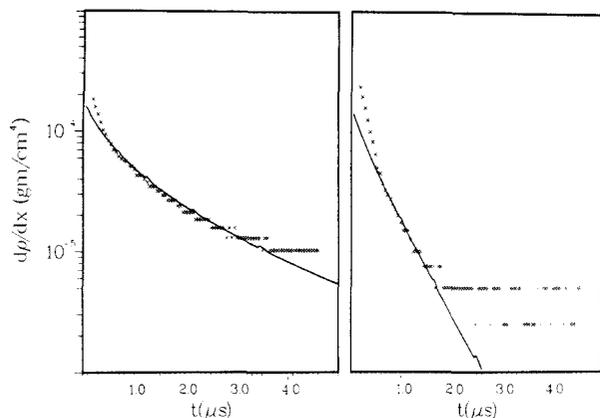


Figure 6. LS semilog density gradient profiles for two high-temperature, high-pressure experiments: 4% VA-Kr, 2218 K, 313 Torr; 2% C₄H₄-Kr, 2470 K, 296 Torr. Data are indicated by ×, and the calculations are as in Figure 4. In the higher temperature experiment, the very slight excess of late gradient may indicate C₄H₂ dissociation.

TABLE III: Example Chain Mechanism

reaction	log A ^a (cgs)	n	E _a , kcal/mol
1. C ₄ H ₄ + M = C ₄ H ₃ + H + M	92.63	-20.5	139.01
2. C ₄ H ₃ = H + C ₄ H ₂	12.60	0.0	40.00
3. H + C ₄ H ₄ = C ₄ H ₃ + H ₂	14.48	0.0	14.50
4. H + C ₄ H ₄ = C ₂ H ₃ + C ₂ H ₂	13.13	0.0	1.38
5. C ₂ H ₃ = C ₂ H ₂ + H	12.95	0.0	43.80
6. C ₂ H ₃ + H = C ₂ H ₂ + H ₂	13.00	0.0	0.00
7. C ₄ H ₃ + H = C ₄ H ₂ + H ₂	13.01	0.0	0.00
8. C ₂ H ₂ + C ₂ H = C ₄ H ₃	13.56	0.0	3.00
9. C ₂ H + C ₄ H ₄ = C ₂ H ₂ + C ₄ H ₃	13.60	0.0	0.00
10. C ₂ H + H ₂ = H + C ₂ H ₂	12.85	0.0	0.00
11. C ₂ H + C ₂ H ₂ = C ₄ H ₂ + H	13.60	0.0	0.00

$$^a \log k = \log A + n \log T - E_a/\theta \quad (\theta = 2.303RT, \text{ kcal/mol}).$$

Example LS density gradient profiles are shown in Figures 4–6. The most important feature of these semilog profiles is immediately evident: *they are all concave-upward*. This behavior is consistent throughout the experiments. Of course those experiments with frozen $T < 1800$ K, where the rate is very low, have nearly flat profiles; but here the concavity must simply be too slight to see.

A concave semilog gradient profile implies the net endothermic rate is decreasing faster than it would from depletion alone. Such profiles can be readily generated by a simple endothermic reaction with positive activation energy whose rate coefficient drops as the temperature falls. An excellent example is the molecular dissociation of cyclohexene to ethylene and 1,3-butadiene.²³ In contrast, when dissociation is the more usual bond fission, the resulting radicals initiate a chain with a consequent acceleration of the endothermic decomposition, and this produces a convex profile. There are many examples of this, among them propane,¹⁷ ethane,²⁸ methanol,²⁹ benzene,³⁰ and acetylene.³¹ In the last two, where dissociation is entirely by C–H scission, the acceleration is so strong it generates a distinct local maximum. The uniform concavity of the VA pyrolysis profiles thus shows *there is no significant chain reaction in the VA decomposition*, and it is then very unlikely the dissociation can be dominated by bond fission.

The likely effect of dissociation by the bond fission of reaction 1, and the sensitivity of the gradient profiles to even a small contribution by such dissociation, are demonstrated by the model calculations of Figures 7 and 8. These calculations use the

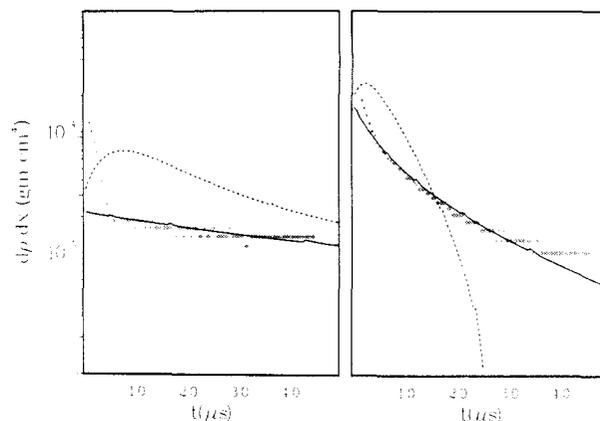


Figure 7. Modeling of two LS semilog gradient profiles from 4% VA-Kr (1768 K, 380 Torr and 2218 K, 313 Torr) with the simple radical chain mechanism of Table III. Here the dashed line shows this calculation, and the solid line repeats the modeling using reaction 12 alone, as previously shown in Figures 4 and 6.

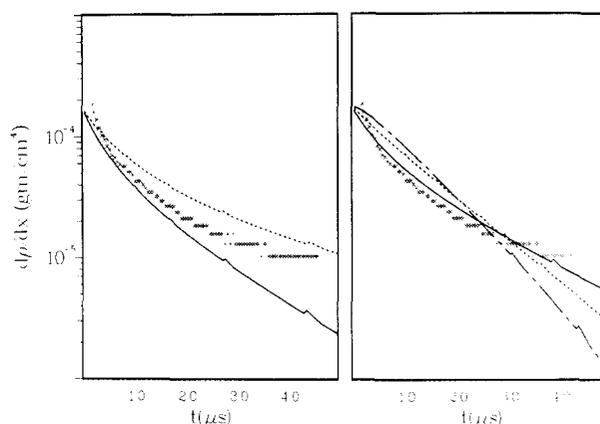


Figure 8. Sensitivity of LS density gradient profiles to heat of reaction and to the introduction of small amounts of the chain mechanism of Table III. In both cases the experiment is the first example of Figure 6. Here the first illustration shows the result of arbitrarily increasing (---) and decreasing (—) the heat of reaction for reaction 12 by 30% in a modeling using that reaction alone. The second example illustrates the results produced by introducing (---) 10%, (---) 5%, and (—) 1% of the VA dissociation via reaction 1, the remainder of the dissociation needed to produce the initial gradients being provided by reaction 12. Reactions 2–11 of Table III are included in these latter calculations.

example chain mechanism listed in Table III, which is just a slightly modified and much simplified version of that proposed by Colket.¹⁴ Here the rate of reaction 1 is based on the LS results (see below) and has been adjusted to give the correct zero-time gradients with this mechanism. Reactions of minor species such as C₆H₆, C₈H₈, C₆H₂, C₈H₂, and the polyacetylene radicals, which will not contribute to the short-time gradient, have been dropped. Actually, with his original k_1 , this simple version does fairly well at reproducing Colket's own calculations of major species concentrations for his single-pulse experiments.

As is evident in Figure 7, even with the initial gradient set appropriately, the prediction of the above chain model is in quite serious disagreement with the observed gradient profiles. We emphasize that this behavior is in no way unexpected. This mechanism is an entirely reasonable notion of what should happen in VA pyrolysis given initiation by reaction 1, and these calculated profiles look much like those actually seen in benzene pyrolysis where initiation is indeed by C–H scission. In fact, not even a small fraction of the chain acceleration generated by this mechanism can be tolerated. The sensitivity study shown in Figure 8 demonstrates that even 1% dissociation through (1) can produce a noticeable deviation.

The LS gradient profiles certainly exclude any significant contribution from chain reaction, but by itself this does not completely prohibit dissociation by bond fission. It is just possible

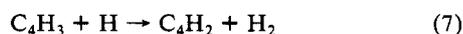
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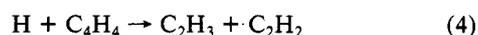
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the chain is quenched by rapid termination. In the mechanism of Table III, and of course the Colket mechanism,¹⁴ an efficient termination can be achieved through the radical-radical disproportionation steps



All that is needed to make these important is a much slower dissociation of either C_4H_3 or C_2H_3 . Certainly for vinyl a slower dissociation seems likely. Colket uses the Benson-Haugen³² estimate which is much faster than the rate recently proposed by Kiefer et al.³³ For the low-pressure LS experiments a slower rate for reaction 5 would be expected in any case, and we have modeled some of the LS experiments with the Table III mechanism inserting the (second-order) rate of vinyl dissociation given by Kiefer et al. This does nearly shut down the chain, and agreement with the LS profiles is much improved. However the fit remains unsatisfactory largely because the effective initial heat of reaction, ΔH for (1) plus (2) or about 147 kcal/mol, is so very large. Also, with the chain blocked, the mechanism now generates approximately equal amounts of acetylene and diacetylene, in complete disagreement with all the product analyses. A fairly long chain is clearly essential for the production of sufficient acetylene in the Colket mechanism. There the acetylene is primarily generated by addition of hydrogen atom to VA, forming C_4H_5 radical which then rapidly decomposes to C_2H_3 and C_2H_2 . In the simplified mechanism of Table III this process is represented by the single reaction



Since the LS profiles exclude significant chain reaction, the large excess of C_2H_2 must arise directly from the dissociation itself; i.e., the dominant channel in this dissociation must be the molecular process



We have accordingly attempted a modeling of the LS profiles using just this reaction alone, with the results shown in Figures 4–6. Here the agreement with the measured gradient profiles is simply excellent, well within expected uncertainty for all the experiments performed. Note that once the rate parameters for (12) have been set to accord with the measured initial (zero-time) gradients, the remainder of each computed profile is completely determined when the mechanism has just this one reaction. The excellent agreement obtained with reaction 12 for all times and all shock conditions again confirms the nonchain nature of the process and also puts the heat of reaction very near that of (12), about 40 kcal/mol.

The sensitivity of the LS gradient profiles to arbitrary variation in heat of reaction is illustrated in Figure 8. Here the ΔH°_{298} for (12) has simply been altered by $\pm 30\%$. To make a "fair" comparison, an opposite change in rate constant was introduced in each case. This preserves the product $r\Delta H$ and thus the zero-time gradient. For either increase or decrease the result is now seen to be a serious deviation. Smaller changes can be roughly compensated by, for example, small shifts in time origin, but it is clear that alterations of 30% or more are unacceptable. Whatever the dissociation channel (or channels) may be, its effective heat of reaction must lie within 30–50 kcal/mol.

The rate constants for reaction 12 obtained from extrapolation of the gradients of each experiment to the time origin are collected in the Arrhenius plot of Figure 9. These rate constants are plotted for second-order reaction, i.e., $\text{M} + \text{C}_4\text{H}_4 \rightarrow 2\text{C}_2\text{H}_2 + \text{M}$. The reaction is evidently well into unimolecular falloff for these conditions and is closer to second order than first. However, there remains a significant separation of high- and low-pressure points so neither extreme strictly applies. For the modeling of Figures 4–6, the somewhat "better" choice of second order was employed.

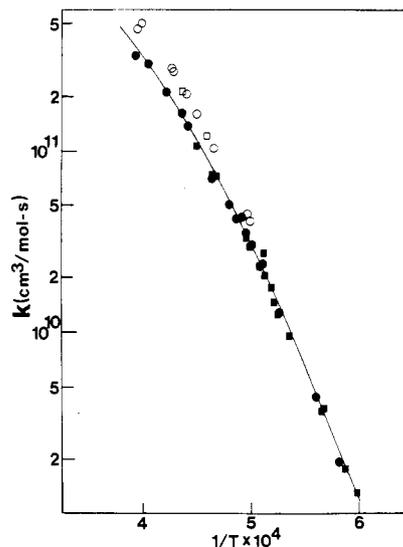


Figure 9. Second-order rate constants for reaction 12 (or for any combination of molecular dissociation reactions with $\Delta H = 40$ kcal/mol) as determined by extrapolation/interpolation of the LS semilog gradient profiles. The experiments are identified as (O) 2% VA-Kr, 125–155 Torr; (□) 4% VA-Kr, 112–130 Torr; (●) 2% VA-Kr, 279–428 Torr; (■) 4% VA-Kr, 312–404 Torr. The solid line shows a least-squares fit of the modified Arrhenius function to the high-pressure points with the result $\log k$ ($\text{cm}^3/(\text{mol}\cdot\text{s})$) = $93.35 - 20.5 \log T - 139.0/\theta$ ($\theta = 2.303RT$ in kcal/mol). This expression was used in the modeling of the experiments of Figures 4 and 6. For the low-pressure experiments of Figure 5 this rate constant was raised by 30%.

TABLE IV: Vibrational Frequencies (cm^{-1}) for "Nonspecific" RRKM Model for Vinylacetylene Dissociation

molecule	transition state	molecule	transition state
300.0	300.0	1100.0	1100.0
620.0	360.0	1310.0	1310.0
680.0	500.0	1410.0	1410.0
930.0	930.0	1600.0	2110.0
970.0	970.0	2110.0	3030.0
220.0	200.0	3030.0	3070.0
540.0	320.0	3070.0	3120.0
620.0	360.0	3120.0	3330.0
870.0	870.0	3330.0	

^aLJ collision parameters (C_4H_4 -Kr): $\sigma = 5.00 \text{ \AA}$, $\epsilon/k = 300 \text{ K}$. One rotation is active, and its moment of inertia is assumed unchanged. The moments of inertia of the two inactive rotations are doubled in the TS. $E_0 = 79.5 \text{ kcal/mol}$, and $-\langle\Delta E\rangle_{\text{all}}$ is a constant 110 cm^{-1} .

The greatest activation energy (E_a) shown by the data of Figure 9, that for the highest pressures and lowest temperatures, approaches 70 kcal/mol. However, given the strong falloff it is likely both the limiting high-pressure activation energy and the barrier are appreciably larger than this. To obtain a better estimate, we have fit an RRKM model to these data with the model parameters listed in Table IV. As usual we have assumed a "nonspecific" vibration model transition state²³ whose frequencies are just those of the molecule,²⁰ save for some of the lower frequencies which have been reduced enough to give a sufficient high-pressure A factor. The parameters seem reasonable, even routine, except for a somewhat large $\langle\Delta E\rangle_{\text{all}}$ (however, this $\langle\Delta E\rangle_{\text{all}}$ corresponds to a $\langle\Delta E\rangle_{\text{down}} \sim 500 \text{ cm}^{-1}$ near 1500 K, which is quite routine³⁴), and the fit in Figure 10 is very satisfactory. This model generates a high-pressure limit rate constant

$$\log k_{\infty,12} (\text{s}^{-1}) = 15.11 - 82.5/\theta \quad (1700\text{--}2400 \text{ K})$$

The measurements are too far into falloff for an accurate extrapolation to k_{∞} , and this A factor is uncertain to at least a factor of 2. However, the calculated rates retain a sensitivity to the barrier at all pressures, so the barrier derived here, $E_0 = 79.5$

(32) Benson, S. W.; Haugen, G. R. *J. Phys. Chem.* **1967**, *71*, 1735.

(33) Kiefer, J. H.; Wei, H. C.; Kern, R. D.; Wu, C. H. *Int. J. Chem. Kinet.* **1985**, *17*, 225.

(34) Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087.

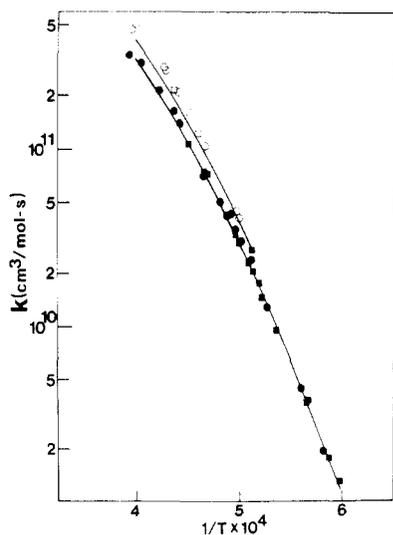


Figure 10. RRKM fit of the rate constants for reaction 12 shown in Figure 9. Here the upper line shows calculations for low pressure, 125 Torr, and the lower line for high pressure, 350 Torr. The model used for these calculations is specified by Table IV.

kcal/mol, should be quite accurate, with an uncertainty of no more than ± 3 kcal/mol.

A modeling of the TOF major species data with the Colket mechanism¹⁴ is shown in Figures 1–3. For these long observation times we have used the full mechanism given by Colket without modification except for a slight reduction in the rate of reaction 1 appropriate for the lower pressures of the TOF measurements. Here the rate constants for (1) are the LS values of Figure 9 reduced by a factor of 3.5, the approximate ratio of the heats of reaction for $C_4H_4 \rightarrow C_4H_2 + 2H$, reactions 1 plus 2, to that for reaction 12. This change gives a rough but reasonable empirical correction for unimolecular falloff of the rate of (1) in the TOF experiments. The TOF and LS experiments use very similar pressures, and with this correction the chain reaction would generate the correct zero-time density gradients.

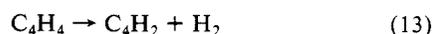
The deviations between measured and calculated VA and C_2H_2 to be seen in Figures 1 and 2 are perhaps not too serious, reflecting mainly a problem with the total rate, but the excessive C_4H_2 in Figure 3, particularly for high temperatures and short times, is not only serious but would be difficult to avoid. These calculations make explicit an essential difficulty with initiation by reaction 1: for high temperatures and short times the products will be dominated by those from initiation and subsequent abstraction reactions, in which case a large and continuing preponderance of acetylene is inexplicable.

Discussion

Previous measurements of the vinylacetylene pyrolysis, taken together with the present LS and TOF measurements, establish the following: (i) the principal products are C_2H_2 and C_4H_2 with a 5–10-fold preponderance of C_2H_2 regardless of rare gas dilution, temperature, or even time; (ii) there is no significant chain reaction in VA pyrolysis at high temperatures; (iii) the heat of reaction, whether from a single step or as an average over parallel channels, is near 40 kcal/mol; (iv) the effective barrier for the dissociation reaction (or reactions) is very close to 80 kcal/mol. Given the absence of chain reaction, the product distribution, and the 40 kcal heat of reaction, the dominant dissociation channel must be



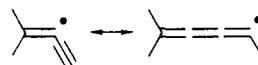
The required C_4H_2 can also be produced without chain reaction and with a heat of reaction again near 40 kcal/mol if we have the parallel channel



Actually, with no chain and the observed products, the heat of reaction *must* be near 40 kcal/mol. The evidence for such a heat of reaction from the LS experiments thus merely shows the

consistency of the observations.

Before any further consideration of the molecular mechanism, we reassemble the arguments against bond fission. For reasons of both entropy and energy, hydrocarbons normally dissociate by C–C scission.³⁵ Such dissociation is, however, excluded in VA because of the great strength of its C–C bonds, a feature it shares with acetylene, ethylene, and benzene. The weakest C–C bond in VA is the central single bond whose dissociation energy, based on the latest values for the heats of formation of C_2H_2 ¹² and C_2H_3 ,¹³ is over 130 kcal/mol. Breakage of this bond cannot possibly make a significant contribution to a dissociation which proceeds rapidly at 1600 K. The only remaining possibility is C–H scission. It seems the interior vinylic hydrogen should be most easily separated from VA, as is routinely assumed,^{11,14,15} because of possible resonance stabilization of the formed C_4H_3



Values suggested for this C–H bond dissociation energy (BDE) range from 79³⁶ to 98¹⁴ kcal/mol. We much prefer the larger value. The “normal” vinylic C–H BDE, that in ethylene, is evidently 103.8 kcal/mol.¹³ Any significant reduction from this in VA must arise from resonance stabilization of the C_4H_3 radical. But these resonance structures do not even have the same minimum-energy nuclear configuration. The resonance energy here should then be much less than it is say in allyl, where it is only 12 kcal/mol.³⁷ It seems most unlikely the bond strength of the C–H bond in VA is under 100 kcal/mol. On this basis we may now estimate a “reasonable” rate for C–H scission in VA. The *A* factor should be under 10^{15} (s^{-1}),²¹ and with $E_a > 100$ kcal/mol, we have $k_\infty < 140 s^{-1}$ at 1700 K, more than 2 orders of magnitude below the k_∞ derived from RRKM extrapolation of the LS data. Note that the strong falloff will favor the lower energy channel even more, since this must completely dominate in the low-pressure limit.

To summarize the case against C–H scission in VA dissociation, we have (i) the evidence against subsequent chain acceleration, (ii) a derived dissociation barrier much below the likely BDE for C–H scission, (iii) the difficulty of producing the large and consistent excess of C_2H_2 over C_4H_2 for all conditions when the dissociation itself produces C_4H_2 , and (iv) the absence of discernible C_4H_3 in the TOF spectra. Unfortunately, C_4H_3 is a major cracking component of the C_4H_4 mass spectrum; nonetheless, no excess C_4H_3 was detectable, and the Colket mechanism applied to the TOF conditions does predict clearly detectable amounts for the higher temperatures.

As we noted earlier, the Colket chain mechanism¹⁴ generates C_2H_2 mainly through the addition–dissociation



overall, reaction 4 of Table III. The rate required for this by the great excess of C_2H_2 observed is $k \sim 10^{13} \text{ cm}^3/(\text{mol}\cdot\text{s})$, a very large rate for addition to an interior carbon.³⁸

Both Colket¹⁴ and Hidaka et al.¹⁵ offer some evidence pointing to chain reaction. Colket’s single-pulse product analyses show traces of methane, ethane, allene–methylacetylene, and even toluene, which almost certainly require the intermediacy of hydrogen atoms in their formation. Only an extremely small amount of H atom is actually needed to produce the trace products in these single-pulse experiments, and this could arise through any or all of (i) a very small fractional dissociation of the VA through C–H scission, (ii) dissociation of easily fissionable impurities like the usual pump oils and perhaps the xylene commonly added as stabilizer to commercial VA, and (iii) dissociation of the products of VA polymerization, for example various C_6H_8 ¹⁰ or larger polymers. Hidaka et al. see some indications of acceleration in

(35) Bradley, J. N. *Proc. R. Soc. London, A* **1974**, *337*, 199.

(36) Cowperthwaite, M.; Bauer, S. H. *J. Chem. Phys.* **1962**, *36*, 1743.

(37) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(38) Tedder, J. M.; Walton, J. C. In *Advances in Physical and Organic Chemistry*; Academic: New York, 1978; pp 16, 51.

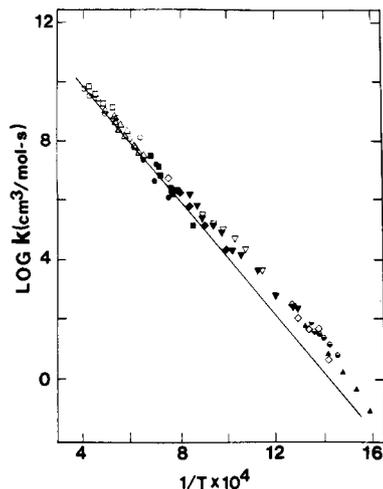


Figure 11. Comparison of calculated detailed balance rate constants (solid line) for the dimerization of acetylene $2\text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$ (VA), reaction -12 of the text, with a schematic presentation (following Palmer and Dormish³) of the extensive literature data for this reaction: (○) ref 41, (□) ref 46 (actually C_2D_2), (△) ref 2, (●) ref 5, (■) ref 42, (◆) ref 4, (▼) ref 3, (▽) ref 43, (◇) ref 44, (⊙) ref 45, (▲) ref 40.

the disappearance of C_4H_4 in their UV absorption measurements. We have no good explanation for this observation, but do note that their profiles show substantial product absorption.

As a final consideration of the previous measurements, we compare the rate coefficients obtained by Colket¹⁴ and Hidaka et al.¹⁵ with those derived from the present LS data. RRKM extrapolation of the LS rate constants to Colket's conditions gives rates about twice those he proposed, but the rate parameters are quite similar. The difference may well come from the additional chain decomposition in Colket's analysis. The LS rates also lie somewhat above those of Hidaka et al. For 1700 K and 300 Torr, the LS rate constant is 5700 s^{-1} and that of Hidaka et al. is 3280 s^{-1} . Again the temperature dependencies are quite close, and we note that a similar disagreement in magnitude exists between LS rate constants and those of these authors for cyclohexene dissociation,³⁹ where they apparently did not take account of temperature drop from the endothermic reaction.²³

If the primary dissociation channel in VA is indeed reaction 12, then its reverse may be the well-known second-order thermal reaction of acetylene. Acetylene pyrolysis behaves as if it were controlled by a single, bimolecular reaction over the entire 600–2500 K range covered by numerous measurements (cf. Figure 11 and ref 5), and there is good evidence that VA is the sole initial gaseous product for moderate temperatures.²⁻⁶ The present results certainly demonstrate that VA can be made by direct dimerization of C_2H_2 , and the only remaining phenomenological issue is then whether this can account for the entire observed second-order rate.

We have calculated equilibrium constants for reaction 12 using the properties of VA and C_2H_2 cited earlier, with a result given closely by

$$\log K_{12} (\text{mol}/\text{cm}^3) = 1.338 - 37.85/\theta$$

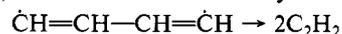
This agrees with the numerical values to within 20% over 700–2400 K. A second-order rate constant for the reverse of reaction 12 may now be calculated from this equilibrium constant and the k_{∞} for (12) derived from the present RRKM calculations. The use of k_{∞} is clearly indicated at low temperatures, and we note that all but one⁴⁶ of the high-temperature shock tube ex-

periments (cited in Figure 11) used the reflected shock with high pressures (see below for further discussion of this matter). The result of this calculation is

$$\log k_{-12} (\text{cm}^3/(\text{mol}\cdot\text{s})) = 13.77 - 44.6/\theta$$

This rate expression for the reverse of (12) is compared to a schematic summary of the numerous measurements of the second-order acetylene reaction in Figure 11. This comparison is really not bad, particularly at high temperatures where a rate derived from the LS data should be most applicable. The calculation is also nearest the homogeneous shock tube data^{2,4,41,46} and the measurements of Palmer and Dormish,⁵ which were corrected for heterogeneous reaction. In any case, the lower temperature rates are just too sensitive to the energies. A reduction of only 1 or 2 kcal/mol in the heat of formation for VA, or similar decrease in the barrier for (12), will produce a very good fit at all temperatures. An error this small in estimated $\Delta H_f^{\circ}{}_{298}$ for VA is obviously possible, as is a similar error in barrier. It seems we must indeed be seeing at least a major part of the second-order reaction of acetylene in the reverse of the vinylacetylene dissociation.

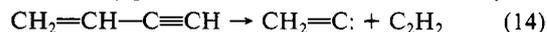
Among many remaining questions are the obvious ones of how reaction 12 can occur and whether reaction 13 is actually a feasible direct process. At first sight dissociation of VA to acetylene would seem to require a prior 1,3-hydrogen shift, in which case a high-pressure A factor around 10^{15} s^{-1} is unexpectedly large. For example, in the extensive examination of the C_4H_4 surface by Kollmar et al.,⁴⁷ the easiest route to acetylene is



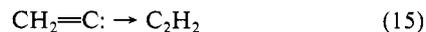
and they estimate a barrier for the reverse of this near the desired 40 kcal/mol. Unfortunately, for this reaction to be rate controlling requires a fast isomerization of VA to the diradical which seems highly unlikely; Kollmar et al. certainly find no such path.

The above dilemma is most easily avoided by having the required hydrogen shift follow the dissociation. We observe that VA is simply a substituted ethylene, which like ethylene itself has no weak bonds, and that the dominant path for ethylene dissociation is known to be the elimination of molecular hydrogen.⁴⁸ This process has been examined theoretically⁴⁹ and evidently involves a 1,1-elimination to singlet vinylidene ($:\text{C}=\text{CH}_2$), followed by very fast isomerization of this to acetylene.⁵⁰⁻⁵² The latest notion of the heat of formation for singlet vinylidene is $\Delta H_f^{\circ}{}_{298} = 97.7 \pm 2 \text{ kcal/mol}$ ⁵³ (actually an upper limit, and lower values have been proposed⁵⁴), 43.5 kcal/mol above acetylene.

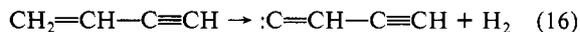
We now propose that dissociation of vinylacetylene, by analogy with ethylene, mainly proceeds via 2,2-elimination of acetylene



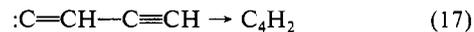
followed by the fast isomerization



and this is reaction 12. This also suggests a path for reaction 13



with fast



(47) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292.

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TABLE V: Transition-State Parameters for H₂ Elimination from C₂H₄

Vibrational Frequencies, ^a cm ⁻¹		
684	1794	530
1000	2802	851
1363	2962	951
1538	3033	

$$(I_x I_y I_z)^{\dagger} = 1431 (\text{amu} \cdot \text{\AA}^2)^3{}^b$$

^a From ref 56. ^b Calculated from structure (no. 5) of ref 49.

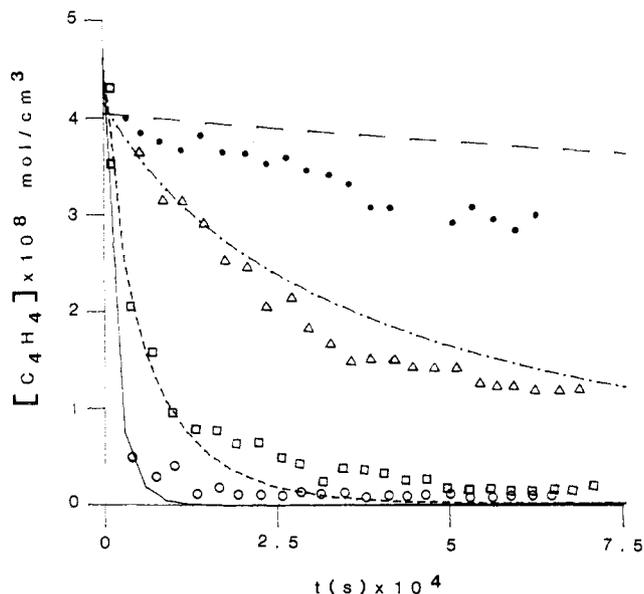
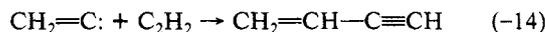


Figure 12. TOF profiles of VA concentration shown in Figure 1 modeled with a simple two-reaction molecular mechanism. Here the total LS rate constants of Figure 9 have been divided 70% for C₄H₄ → 2C₂H₂ and 30% for C₄H₄ → C₄H₂ + H₂. The lines and symbols are identified as they are in Figure 1. The reason for the inadequate conversion at 1492 K is not known.

The dissociations are thus inverse vinylidene insertions,⁵⁵ and this suggestion obviously entails the notion that the bimolecular reaction of acetylene is largely the insertion



Given fast reaction 15, the vinylidene will be steady state, and the rate constant for the reverse of (12) will remain $k_{-12} = k_{12}/K_{12}$, since k_{14} is now the forward rate constant for (12).

The inverse vinylidene insertion mechanism for VA dissociation has the right energetics and can also provide a reasonable explanation for the large *A* factor. The heat of reaction for (14) is $\Delta H^\circ_{298} = 54.2 + 97.7 - 69 = 84.9$ kcal/mol and should be about 83 kcal/mol at 0 K. If we now make the reasonable assumption of near-zero barrier for the reverse of (14), this ΔH°_0 should be close to the barrier for reaction 12 derived from the LS data, $E_0 = 79.5$ kcal/mol. Considering that the heat of formation for vinylidene used here is an upper limit, the agreement is excellent.

The question of whether the large high-pressure *A* factor is "reasonable" is rather more difficult since the only extant example of the inverse of a vinylidene insertion into a single bond is ethylene dissociation, where the reaction is near the low-pressure limit in the experiments.^{25,48} However, the properties of the transition state for 1,1-elimination of H₂ from C₂H₄ have been characterized theoretically^{49,56} and are given in Table V. We have used these parameters to calculate a TST k_∞ with the result

$$\log k_\infty (\text{s}^{-1}) = 14.32 - 87/\theta \quad (1700-2400 \text{ K})$$

(55) Berson, J. A. In *Rearrangements in Ground and Excited States*; Academic: New York, 1980; p 311. See also: Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(56) Pople, J. A., private communication.

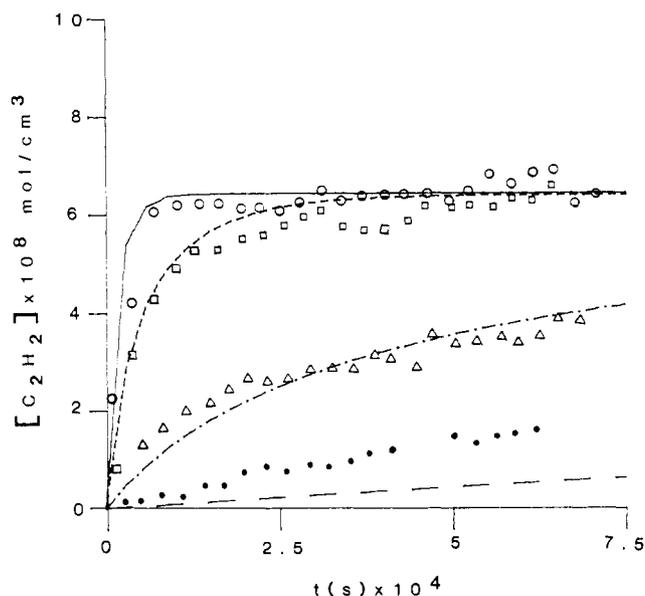


Figure 13. TOF profiles of C₂H₂ concentration of Figure 2 modeled with the simple molecular mechanism of Figure 12. Data and calculations are identified as in Figure 12.

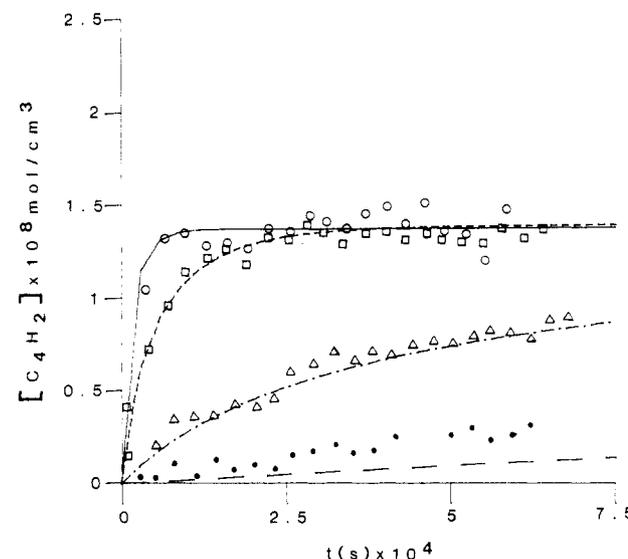


Figure 14. TOF profiles of C₄H₂ concentration of Figure 3 modeled with the simple molecular mechanism of Figure 12. Data and calculations are identified as in Figure 12.

Here the barrier was chosen as 83.4 kcal/mol, so the effective E_a lies 3.5 kcal/mol higher. This difference reflects an almost T^{-1} dependence of the frequency factor, arising mainly from kT/h , which must be recognized when comparing values from different temperatures.

The high-pressure *A* factors for the ethylene and VA inverse insertion (dissociation) rates refer to the same temperature range and may be fairly compared. The ratio of these is ~6 with an uncertainty of at least a factor of 2. There thus has to be 2 or 3 eu additional ΔS^\ddagger for C₂H₂ elimination from VA, part of this because ethylene has a factor of 2 advantage from reaction path degeneracy which must also be made up. Still, this does not sound unlikely since a much more massive group is being separated, with a greater increase in transition-state moments of inertia, as well as the reduction of lower frequencies. The 3–5 times smaller rate for (13) indicated by the measured C₂H₂/C₄H₂ ratios could then be ascribed almost entirely to the frequency factor for (12) and (13). This would leave these two reactions with nearly identical barriers, and this is not only what one would expect from the rate-controlling reactions 14 and 16, but it is also entirely consistent with the remarkable constancy of these product ratios.

Since reactions 12 and 13 both have heats of reaction near 40 kcal/mol, any combination of these two processes with the right total rate—the rate given by the total rate constants of Figure 9—will fit the LS data. The measured C_2H_2/C_4H_2 product ratios would thus imply about 70–83% of the total LS rate constant for k_{12} and the remainder for k_{13} . In Figures 12–14 we show that the TOF species profiles are generally well-described by the simple combination of reactions 12 and 13 with such rate constants. This agreement is in rather stark contrast to the large deviations shown by the earlier modeling with the chain mechanism illustrated in Figures 1–3.

The pleasing agreement at high temperatures in Figure 11, i.e., that between the computed rate constants for the reverse of reaction 12 and the collected measurements, now seems rather misleading. Some of the LS rate has been assigned to reaction 13, and the use of k_{12} for (12) is really not appropriate for $T > 1500$ K; even for the high (3–10 atm) pressures used in the single-pulse work the RRKM model predicts a 30–50% falloff at 1500 K. However, the falloff problem may actually be somewhat ameliorated by the additional dissociation channel, reaction 13. With a similar barrier for both (12) and (13), one would expect a direct conversion of C_2H_2 to C_4H_2 for low pressures (or high temperatures) as $2C_2H_2 \rightarrow C_4H_2 + H_2$. This may explain the change of dominant product from VA to C_4H_2 which evidently occurs in C_2H_2 pyrolysis around 1500–1600 K.^{4,5,14} For this, or still higher temperatures, some dissociation of the hot C_4H_4 adduct to $C_4H_3 + H$ should also occur, initiating further chain reaction. These processes will act to “pull” the dimerization forward, at least partially compensating the falloff in VA formation. This may still leave the rate a bit low, but there are other mitigating considerations.

There is usually much more to C_2H_2 pyrolysis than a simple dimerization to VA or even to $C_4H_2 + H_2$. At the lowest temperatures (~ 700 K) the principal product is polymer,⁴⁰ at higher temperatures it can be benzene,^{3,7} and at very high temperatures higher polyacetylenes are generated.¹⁴ Some of the many products of this pyrolysis may arise without the intervening formation of VA. Certainly at very high temperatures there is a major contribution from a strongly branched chain which is probably initiated by acetylene dissociation.^{25,31} At lower temperatures it seems

the reaction is partially heterogeneous,⁵ and impurities could easily generate significant chain reaction. Some polymer may be generated without prior formation of VA. The reaction of 1,1-diradicals with unsaturated hydrocarbons is usually dominated by insertion into a multiple bond.⁵⁵ If this is true also of vinylidene and acetylene, then formation of methylenecyclopropene would be expected. Methylenecyclopropene has now been synthesized^{57,58} and is found to be quite unstable even at very low temperatures. For one thing it apparently polymerizes,⁵⁸ and this might account for some of the polymer seen in C_2H_2 pyrolysis. At higher temperatures it probably reverts to C_2H_2 .

Finally, one further consideration of the relation between ethylene and VA dissociation is worthwhile. For ethylene a contribution from C–H bond fission and consequent chain acceleration is clearly evident in the LS experiments.^{25,48} However, these were confined to $T > 2000$ K where such fission is approaching 10% of the total dissociation, whereas at 1800 K the fission channel has only about 1% the rate of the molecular process. The absence of discernible chain reaction in VA pyrolysis must then be because the larger VA molecule shows less falloff and thus a measurable rate at lower temperatures, favoring the lower barrier molecular channels. The molecular channels also have about a factor of 6 larger high-pressure A factor in VA, and enough of this high-pressure rate remains to favor these even more.

Since this work was submitted, a paper by Duran et al.⁵⁹ has appeared in which they also propose that acetylene dimerizes through a vinylidene insertion, and they offer additional independent evidence for this mechanism.

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Excited-State Proton-Transfer Kinetics: A Theoretical Model

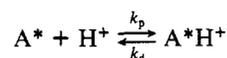
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The intersecting-state model is applied to excited-state proton-transfer reactions. The results are consistent with those previously obtained for the analogous ground-state reactions. The transition-state bond order n^\ddagger is similar in the ground and excited states: carbon acids have lower n^\ddagger than nitrogen or oxygen acids. The mixing entropy parameter λ is found to be lower for excited-state than ground-state reactions. The mechanistic implications of this are discussed.

Overview

Proton-transfer reactions are one of the most fundamental processes in chemistry. As early as the 1950s the basic differences between proton transfers in ground and excited states were established by Förster and Weller.^{1–3} Since then many studies have been made to better understand the energetic and kinetic differences between these systems, through determination of chemical equilibrium constants (pK_a^*), and protonation and deprotonation excited-state rate constants (k_p , k_d):



Although such studies were made for a large number of species,^{4,5} quantitative theoretical predictions of k_p and k_d from thermodynamic and molecular data did not emerge from the available studies for many years. Meanwhile, the kinetics of the ground-state proton transfers were interpreted mainly through the theory of Marcus.^{6–8} Until very recently no attempt was made

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