J. Phys. Chem. 1988, 92, 636-640

Is the Homogeneous Thermal Dimerization of Acetylene a Free-Radical Chain Reaction? Kinetic and Thermochemical Analysis

R. P. Durân, V. T. Amorebieta, and A. J. Colussi*

Department of Chemistry, University of Mar Del Plata, 7600 Mar Del Plata, Argentina

(Received: September 23, 1986)

Basic kinetic and thermochemical arguments incorporated into calculations modeling the initial stages of the homogeneous pyrolysis of acetylene reveal that the usual assumption of a free-radical mechanism is flawed. The key findings are that updated thermochemistry for ethynyl, vinyl, and propargyl radicals and the inclusion of falloff corrections in radical reactions lead to (1) exceedingly slow decomposition rates below 1300 K, (2) kinetic inert gas effects, and (3) the formation of benzene rather than vinylacetylene or diacetylene, all predictions at variance with experimental observations. On this basis the involvement of vinylidene is proposed.

Introduction

Acetylene has long been identified as a major component of flames and more recently as the species responsible for the growth of soot particles.[1] However, and despite much effort, the basic mechanism for the thermal decomposition of this simple hydrocarbon is still not well established. This assertion is very puzzling after considering the apparent agreement among numerous studies performed by vastly different techniques covering the range 625–3400 K.[2] Thus, second-order rate constants, which can be retrieved up to 40% acetylene conversion seem to fit reasonably well the Arrhenius expression: $\log k\ (\mathrm{M^{-1}\ s^{-1}}) = 10.8 - 41.6/\theta$ ($\theta = (4.575 \times 10^{-3})\ T$ kcal/mol), do not display third-body effects, and are rather insensitive to walls and to most additives, with the exception of free-radical scavengers such as NO.[3,4] Careful chemical analysis reveal that vinylacetylene is the initial product although diacetylene, methane, H_2, benzene, and carbon deposits are formed at later stages, particularly at high temperatures.[3] Such observations have led in the past to assume a single free-radical chain mechanism encompassing all experimental conditions.[2,5] Finding a plausible initiation reaction is at the core of the problem since unimolecular dissociation of acetylene is ruled out both by the observed second order and the lack of inert gas affects and by the extremely large value of the C–H bond energy: BDE(HCC–H) = 125 kcal/mol.[6]

In this paper we show that the apparent success of previously proposed free-radical mechanisms relies critically on early data for the heats of formation of intermediate vinyl, ethynyl, and propargyl-type radicals, now known to be seriously in error, as well as on the arbitrary assignment of falloff effects for radical addition, decomposition, and combination reactions.[7-9] Given the importance of the issue, we have now undertaken model calculations on revised schemes properly dealing with such features. As it emerges, conceivable free-radical mechanisms comprising homogeneous bimolecular initiation and termination reaction leading to overall second order turn out to be otherwise inconsistent with the described kinetic behavior below ca. 1500 K to such an extent that they may be safely disregarded.

We then proceed to argue that the pyrolysis of acetylene actually begins with its reversible isomerization into singlet vinylidene followed by addition reactions of the carbene. At least three independent pieces of information seem to support this proposal. The first one is that ab initio calculations actually predict a value for the heat of formation of vinylidene ca. 40 kcal/mol above that of acetylene, as required.[10,11] Moreover, recent studies of the thermal reactions of acetylene with benzene and toluene reveal that they lead to addition, instead of radical-displacement, products with second-order rate constants almost identical with the one determined in neat acetylene at the same temperatures.[12] Both observations are entirely consistent with the involvement of a common nonradical reactive intermediate. Finally, the recently invoked nascent formation of vinylidene in the high-temperature decomposition of methylenecyclopropane, from which an upper limit of $\Delta H_f(H_2C{=}C{:}) = 98$ kcal/mol was derived, lends verisimilitude to its existence as a discrete kinetic species.[13]

It should be emphasized that no attempt has been made here to account for the diversity of products formed in acetylene pyrolysis under all experimental conditions, a task that almost certainly must include secondary processes such as the decomposition of the less stable vinylacetylene as well as the sequential addition of acetylene to unsaturated intermediate species.[12,14] Although of possible practical interest, it is felt that such an endeavor would obscure rather than clarify the mechanism of acetylene pyrolysis.

Chain Mechanisms

Application of the general theory of homogeneous chain processes to acetylene pyrolysis indicates that the combination of bimolecular radical termination reactions and overall second order demands bimolecular initiation and propagation steps.[15] Two thermodynamically feasible initiation reactions belong to the required category, namely, molecular disproportionation and concerted addition with bond fission. The former reaction has been proposed by Back:[2]

$$2C_2H_2 = C_2H_3 + HC_2 \tag{21}$$

and the latter by Tanzawa and Gardiner, following Kistiakowsky et al.:[5,16]

$$2C_2H_2 = C_4H_3 + H \tag{2}$$

where C_4H_3 stands either for a vinyl, $HC{\equiv}C{-}CH{=}\dot{C}H$, or a more stable propargyl, $CH{\equiv}C{-}\dot{C}{=}CH_2$, radical. Reaction must

---

(1) Harris, S. J.; Weiner, A. M. *Annu. Rev. Phys. Chem.* **1985**, *36*, 31.

(2) Back, M. H. *Can. J. Chem.* **1971**, *49*, 2199.

(3) Cullis, C. F.; Franklin, N. H. *Proc. R. Soc. London, A* **1964**, *280*, 139.

(4) Ogura, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1044; *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3418.

(5) Tanzawa, T.; Gardiner, W. C. *J. Phys. Chem.* **1980**, *84*, 236.

(6) Wodtke, A. M.; Lee, Y. T. *J. Phys. Chem.* **1985**, *89*, 4744 have derived an even larger value of $\Delta H_f(HC_2) = 134$ kcal/mol, i.e., $BDE(HC_2{-}H) = 131.9$ kcal/mol.

(7) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 439.

(8) (a) Colussi, A. J. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z., Ed.; CRC: Boca Raton, FL, 1987; Chapter 3. (b) Shiromara, H.; Achiba, Y.; Kimura, K.; Lee, Y. T. *J. Phys. Chem.* **1987**, *91*, 17, have just measured $\Delta H_f(C_2H_3) = 77.0$ kcal/mol.

(9) Dean, A. M. *J. Phys. Chem.* **1985**, *89*, 4600.

(10) Scheiner, A. C.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1985**, *107*, 4451.

(11) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603.

(12) Durân, R. P.; Amorebieta, V. T.; Colussi, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3154.

(13) Davison, P.; Frey, H. M.; Walsh, R. *Chem. Phys. Lett.* **1985**, *120*, 227.

(14) (a) Lundgard, R.; Heicklen, J. *Int. J. Chem. Kinet.* **1984**, *16*, 125. (b) Chanmugathas, C.; Heicklen, J. *Int. J. Chem. Kinet.* **1986**, *18*, 701. (c) Hidaka, Y.; Tanaka, K.; Suga, M. *Chem. Phys. Lett.* **1986**, *130*, 195.

(15) Huyser, E. S. In *Physical Chemistry, An Advanced Treatise*; Academic: New York, 1975; Vol. VIII, p 299.

(16) Gay, I. D.; Kistiakowsky, G. B.; Michael, J. V.; Niki, H. *J. Chem. Phys.* **1965**, *43*, 1720.

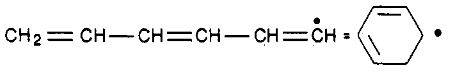
0022-3654/88/2092-0636$01.50/0

TABLE I: Thermodynamic Data

species	$\Delta H_f°$ at 300 K, kcal/mol	$S°$ at 300 K, eu	$C_p°$, eu 100 K	200 K	300 K	400 K	500 K	700 K	1000 K	1300 K
C_2H_2[a]	54.2	48.1	7.0	8.5	10.6	12.1	13.1	14.6	16.3	17.6
C_4H_4[a]	72.8	66.9	10.4	14.0	17.6	21.3	24.3	28.7	33.2	36.3
C_4H_2[a]	13.0	59.9	7.7	13.2	17.1	20.2	21.9	24.2	26.6	28.8
C_6H_6[a]	19.8	64.5	8.4	12.8	19.7	26.7	32.8	41.8	50.2	53.3
C_2H_4[a]	12.5	52.5	8.0	8.5	10.5	12.9	15.2	18.8	22.6	25.1
$^\bullet C_2H$[b]	127	49.6	7.0	7.8	8.9	9.7	10.2	11.1	12.2	12.9
$^\bullet C_2H_3$[c]	70(a) 64(b)	56.3	8.0	8.4	9.7	11.5	13.1	15.8	18.6	20.5
$^\bullet C_4H_3$[d]	130(a) 124(b)	66.1	10.4	13.8	16.9	19.7	22.1	25.7	29.3	31.7
$^\bullet C_4H_5$[e]	84(a) 78(b)	69.1	10.4	14.0	18.6	23.0	26.7	32.4	38.2	41.5
$^\bullet C_6H_7$[f]	49.9	72.1	9.9	13.7	20.8	28.4	35.1	45.0	54.4	60.1
$^\bullet C_6H_5$[g]	78.5	69.4	8.2	12.5	18.8	25.4	30.3	39.0	46.4	50.9
$^\bullet C_4H$	185.8	62.1	7.6	12.0	15.3	17.3	18.7	20.7	22.6	23.0
H	52.1	27.7	5.0							5.0

[a] Reference 40. [b] Reference 21. [c] (a) Values from ref 7; (b) values from ref 20. [d] $HC\equiv C-CH=\dot{C}H$; for the secondary radical formed in reaction 2 (Table III) subtract 10 kcal/mol from $\Delta H_f°$. [e] $CH_2=CH-CH=\dot{C}H$. [f] Cyclohexadienyl; reference 35. [g] Reference 7.

then proceed along standard propagation steps such as radical decomposition or addition to acetylene. Since small radicals are involved, such propagation reactions are expected to display severe falloff effects under all experimental conditions. Alternative H-atom abstractions from acetylene are at least some 20 kcal/mol endothermic for the most reactive vinyl radicals and hence do not compete with addition reactions. Radical isomerizations such as H-atom intramolecular shifts or skeletal rearrangements deserve further comment. The former would lead to more stable radicals, i.e., to species more liable to undergo addition than decomposition reactions, thereby increasing the yield of higher molecular weight products. As shown below, mechanisms omitting radical isomerization already predict benzene to be the major product and therefore its inclusion was deemed unnecessary. Although they have not been directly investigated, isomerization of C_6 linear unsaturated vinyl radicals into cyclic allylic species is so favorable that they should readily take place. Thus, for example, the reaction



is about 50 kcal/mol exothermic, and as a consequence we consider $C_6H_7^\bullet$ as a cyclohexadienyl radical all along.

Kinetic and Thermochemical Parameters

For the sake of consistency, a common set of kinetic parameters have been chosen for each class of addition reaction. The *A* factors are assigned the values $10^{8.3}$, $10^{8.8}$, and $10^{9.3}$ M^{-1} s^{-1} according to whether none, one, or both reacting species are linear.[17] The special cases of atom addition to linear and nonlinear species are well documented, and typical values of $10^{10.0}$ and $10^{9.7}$ M^{-1} s^{-1} are adopted here, respectively. The corresponding activation energies, on the other hand, have been classified as addition of H atoms or vinyl-type radicals to alkynes. Whereas we have chosen the experimental value of $E = 2.8$ kcal/mol in the former case,[18] a value of $E = 4.9$ kcal/mol has been derived for the addition of vinyl radicals to alkynes from recent measurements of the relative rates of $C_2H_3 + H_2$ and $C_2H_3 + C_2H_2$ reactions after being scaled up to our assignment of *A* factors.[19] Upper limits for radical combination plus disproportionation rate constants have been taken as one-fourth of collision rates at each temperature.[17] The parameters for the reverse dissociation of free radicals and stable molecules have then been evaluated by detailed balance from the above estimates and thermochemical data in Table I.[17] It should be emphasized that since the reverse of reaction 2 is not a simple recombination, E_2 is necessarily larger than ΔH_2.

TABLE II

	vibrational frequencies, cm^{-1}	E_z, kcal/mol	β[a]
C_2H_2[b]	3374 (1), 1974 (1), 3282 (1), 612 (2), 729 (2)	16.2	1.307
C_4H_4	3200 (2), 3300 (2), 1650 (1), 1974 (1), 1000 (3), 300 (2), 1100 (4), 600 (2), 150 (1)	37.1	1.452
C_4H_2	3300 (2), 1974 (2), 440 (4), 550 (4), 950 (1)	22.1	1.630
C_6H_6	3100 (6), 410 (2), 606 (2), 1486 (2), 1596 (2), 849 (2), 975 (2), 1038 (2), 1178 (2), 703 (1), 1010 (1), 992 (1), 1310 (1), 613 (1), 995 (1), 1150 (1), 1362 (1)	61.5	1.336
C_2H_4	3100 (4), 1650 (1), 1150 (4), 1450 (2), 450 (1)	31.5	1.156
C_2H	1920 (1), 640 (2), 3220 (1)	9.2	1.082
C_2H_3[c]	779, 1002, 1017, 1257, 1386, 1656, 3157, 3268, 3369	24.1	1.146
C_4H_3	3200 (2), 3300 (1), 1650 (1), 1974 (1), 1000 (1), 300 (2), 1100 (4), 600 (2), 150 (1)	29.6	1.466
C_4H_5	2800 (5), 1650 (2), 800 (1), 1200 (4), 900 (3), 150 (1), 300 (2), 750 (3)	40.9	1.354
C_6H_7[d]	106 (1), 410 (1), 630 (1), 640 (1), 650 (1), 1035 (1), 956 (1), 1620 (1), 1358 (3), 1650 (1), 700 (1), 706 (1), 920 (2), 950 (3), 1100 (1), 1130 (1), 1150 (1), 1159 (1), 1197 (1), 1420 (1), 1450 (1), 2822 (1), 2875 (1), 2877 (1), 3077 (1), 3019 (1), 3032 (2)	67.5	1.319
C_6H_5	3150 (5), 475 (2), 606 (2), 1486 (2), 1596 (2), 849 (2), 995 (3), 1178 (2), 1362 (1), 1150 (1), 613 (1), 1310 (1), 992 (1), 1010 (1), 703 (1)	54.7	1.337
C_4H	3300 (1), 1974 (2), 950 (1), 440 (4), 550 (2)	15.8	1.543

[a] $\beta = [(s-1)/s](\langle\nu^2\rangle/\langle\nu\rangle^2)$. [b] Reference 34. [c] Adapted from ref 41. [d] From ref 35.

The crucial value of the heat of formation of the vinyl radical has been set at 70 kcal/mol in agreement with iodination and proton affinity studies.[7,8] Nevertheless, the lower value of $\Delta H_f(C_2H_3) = 64$ kcal/mol preferred by Back, which yields much faster pyrolysis rates, has also been tested.[20] Several independent determinations of the heat of formation of the ethynyl radical appear to converge to the value $\Delta H_f(HC_2) = 134$ kcal/mol recommended by McMillen and Golden.[6,7] We have adopted here a conservative lower limit of 127 kcal/mol which obviously represents the most favorable choice for reaction 21.[21] Propargyl-type radicals, such as the above-mentioned but-1-en-3-yn-2-yl radical, have been dealt with by assuming that they are stabilized by about 10 kcal/mol as in the prototype propargyl radical itself, $^\bullet CH_2-C\equiv CH$.[22] Entropies and heat capacities of radicals have been

---

(17) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(18) Payne, W. A.; Stief, L. J. *J. Chem. Phys.* **1976**, *64*, 1150.

(19) Callear, A. B.; Smith, G. B. *Chem. Phys. Lett.* **1984**, *105*, 119.

(20) Ayranci, G.; Back, M. H. *Int. J. Chem. Kinet.* **1983**, *15*, 83.

(21) Frank, P.; Just, Th. *Combust. Flame* **1980**, *38*, 231.

estimated from reported data for the parent molecules by the difference method.[17]

Vibrational frequencies have been taken from the literature when available or have been estimated by adjusting generic local mode frequency assignments in Table II to overall vibrational heat capacities: $C_{vib} = C_p - 8$, both at 300 and 1000 K.

Falloff Corrections and Lifetimes of Chemically Activated Species

The degree of falloff in radical addition, decomposition, and combination reactions, such as in $H + C_2H_2 = C_2H_3$, $C_4H_3 = C_4H_2 + H$, and $C_4H_3 + H = C_4H_4$, respectively, has been estimated by the method of Troe.[23] It basically consists of calculating k_0 and k_∞, the limiting low- and high-pressure rate constants for each reaction. The former is easily derived from the factored expression of k_0:

$$k_0 = [M]\beta_c Z_{LJ} \frac{\rho_{vib,h}(E_0)kT}{Q_{vib}} \exp(-E_0/kT) F_{anh} F_E F_{ext\ rot} F_{int\ rot} F_{corr} \qquad (I)$$

whose input data are either given in Tables I and II or taken from the literature. Symbols adhere fully to Troe's notation.[23] Collision efficiencies β_c fall in the range 0.1–0.3 for all species if typical values of $\langle \Delta E \rangle$ for argon as the bath gas are used.[24] In all cases the external rotation $F_{ext\ rot}$ factor was close to 1 due to the fact that moments of inertia barely change for H-atom fission in free radicals. E_0 was arbitrarily taken as $E_\infty - 1$ for the tight transition states involved.

The rates of decomposition of chemically activated free radicals such as $C_4H_5^*$, $C_6H_7^*$, and $C_4H_3^*$ (from $C_2H + C_2H_2$) along the various possible reaction channels were simply estimated from Forst's expression:

$$k(E) = A_\infty \left[\frac{E - E_0 + a'E_z}{E + aE_z} \right]^{s-1+0.5r} \qquad (II)$$

with $E = -\Delta H_0° + E_{th} + E_{act} - 3RT$, the average vibrational energy deposited in the radical adduct, which uses the Whitten–Rabinovitch approximation to calculate the density of states $N(E)$.[25,26] This approach provides a straightforward yet realistic procedure for the evaluation of the relative rates of back and forward dissociation vs collisional stabilization. It should be pointed out that this approximation gave a degree of falloff within 20% of the one estimated by means of eq I for $H + C_2H_2$ and is therefore considered reliable for present purposes. In any event it can be shown that moderate (50%) variations of estimated lifetimes have only a marginal influence on overall rates for reasons that will become apparent in the discussion below. Rates of all reactions considered at 700, 1000, and 1300 K for a 10% mixture of C_2H_2 in argon at total pressures of 0.1 and 1 atm are presented in Table III. For those reactions in which two values appear, the upper (lower) one corresponds to the adoption of $\Delta H_f(C_2H_3)$ = 70 (64) kcal/mol, respectively, and is labeled with a (b) in the text.

Model Calculations

Integration of the sets of differential equations for mechanisms involving the sequences: of mechanism 1a(b), reactions 2–16, 23, and 24; mechanism 2a(b), reactions 3–11, 13, 15, 16, and 18–25; and mechanism 3a(b), mechanism 1 plus reactions 17 and 22 was performed at the six experimental conditions of Table III by means of HICHM, a Fortran code for the Gear algorithm, run on a HP-1000 computer.[27]

Results and Discussion

It seems necessary to start with an analysis of the assumptions and conclusions derived from the mechanism recently put forward by Tanzawa and Gardiner for the pyrolysis of acetylene between 625 and 3400 K.[5] We chose to confine the discussion to temperatures below 1300 K where the unimolecular dissociation of acetylene becomes much slower than putative bimolecular initiations (Table III, reaction 1).[28] Under these conditions the contracted Tanzawa and Gardiner mechanism reduces to the reactions (rate constants in $mol^{-1}\ dm^3\ s$)

$$C_2H_2 + C_2H_2 = C_4H_3 + H \qquad \log k_a = 9.3 - 45.9/\theta \qquad (a)$$

$$C_2H_2 + H = C_2H_3 \qquad \log k_b = 9.7 - 2.4/\theta \qquad (b)$$

$$C_2H_2 + C_2H_3 = C_4H_4 + H \qquad \log k_c = 9.2 - 25.1/\theta \qquad (c)$$

$$C_4H_3 + H + M = C_4H_4 + M \qquad \log k_d = 9.0 \qquad (d)$$

$$C_4H_3 + M = C_4H_2 + H + M \qquad \log k_e = 13.0 - 59.8/\theta \qquad (e)$$

Comparison of the preceding Arrhenius expressions and derived rates with the data in Tables I and III reveals that (1) the activation energy of reaction a is about 14 kcal/mol lower than allowed by the most favorable thermochemistry of vinyl radicals, (2) the degree of falloff of reactions b, d, and e is grossly misassigned with formation of vinyl reaching deep in it, particularly at 1300 K, 0.1 atm and the rest closely approaching their high-pressure limits, and (3) reaction c is unrealistic as written since the likely intermediate, $C_4H_5^*$ radicals, would rather stabilize than decompose under typical experimental conditions. Moreover, the numerical integration of the above mechanism, or the complete one for that matter, indicates that it *even fails to reproduce the observed second order up to 50% conversions, although initial rates are admittedly proportional to the square of acetylene concentration* (Figure 1a). Instead it can be shown that a plot of $C_{C_2H_2}^{1/2}$ vs time is nearly linear beyond about 5% conversions, revealing a basic shortcoming of the whole model.

We have then proceeded to integrate mechanisms starting with reactions 2 or 21 for both choices of ΔH_f(vinyl). Noteworthy is the fact that the vinyl radical chain only regenerates H atoms at appreciable rates in the decomposition of hot cyclohexadienyl radicals, $C_6H_7^*$, (Table III, reaction 10), for this is the only step fast enough to compete with collisional deactivation. The net effect is that whereas decomposition rates barely change since H-atom addition to acetylene remains the slow propagation step throughout, the chain now leads to benzene rather than vinylacetylene as the main product. We have investigated this point in more detail by including the exothermic H-atom transfer between $C_4H_5^*$ and C_2H_2:

$$C_4H_5^* + C_2H_2 = C_2H_3 + C_4H_4 \qquad (17)$$

with $\Delta H_{17} = -35.6$ kcal/mol, which would effectively bypass the loop $C_2H_3 \rightarrow C_4H_5^* \rightarrow H \rightarrow C_2H_3$. However, it was found that even at the fastest possible rate, reaction 17 has but a marginal effect on the overall behavior of any of the tested mechanisms. Of course, this is a consequence of the fact that $C_4H_5^*$ would deactivate in collisions with excess argon rather than react with acetylene via reaction 17. In any event, the insensitivity of manometric measurements of acetylene decomposition rates to the addition of inert gases strongly argues against a change of stoichiometry.[3] In all cases the calculated $1/C_{C_2H_2}$ vs time plots were linear (Figure 1b) but the derived second-order rate constants were considerably smaller than experimental values, the discrepancy worsening at lower temperatures (Figure 2). It is also evident that the log k vs $1/T$ plots deviate from Arrhenius behavior and moreover that they are pressure dependent. As expected, the fastest rates are obtained with initiation 2 (mechanisms 1 and 3).

---

[22] King, K. D.; Nguyen, T. T. *J. Phys. Chem.* **1979**, *83*, 1940.

[23] Troe, J. *J. Phys. Chem.* **1979**, *83*, 114.

[24] Quack, M.; Troe, J. In *Gas Kinetics and Energy Transfer*, The Chemical Society: London, 1977; Vol. 2, 175.

[25] (a) Forst, W. *J. Phys. Chem.* **1972**, *76*, 3421. (b) Colussi, A. J.; Cvetanovic, R. J. *J. Phys. Chem.* **1975**, *79*, 1891.

[26] Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: London, 1972; Chapter 5.

[27] Brown, R. L. HICHM: *A Fortran Code for Homogeneous, Isothermal Chemical Kinetics Systems*; U.S. Department of Commerce. NBS: Washington, DC, 1981; NBSIR 81-2281.

[28] These values for reaction 1 have been extrapolated from data in ref 21 according to the methods of ref 23.

TABLE III: Rate Constants at Total Pressures of 0.1 and 1 atm[a]

no.	reaction	700 K	1000 K	1300 K	ref and notes
1	$C_2H_2 = C_2H + H$	2.7 (−23),[b] 2.7 (−22)[c]	2.0 (−13),[b] 2.0 (−12)[c]	4.7 (−9),[b] 4.7 (−8)[c]	21, 23
2	$C_2H_2 + C_2H_2 = C_4H_3{}^d + H$	2.0 (−11)	2.0 (−5)	3.4 (−2)	$A_2 = 10^{9.3}$
		1.6 (−9)	4.2 (−4)	3.5 (−1)	
3	$H + C_2H_2 = C_2H_3$	2.2 (7),[b] 1.3 (8)[c]	2.0 (7),[b] 1.5 (8)[c]	1.3 (7),[b] 1.1 (8)[c]	18, 23
		4.2 (7),[b] 2.0 (8)[c]	2.8 (7),[b] 2.0 (8)[c]	1.9 (7),[b] 1.3 (8)[c]	
4	$C_2H_3 + C_2H_2 = C_4H_5{}^*$	1.9 (7)	5.4 (7)	9.5 (7)	
5	$C_4H_5{}^* = C_2H_3 + C_2H_2$	6.0 (7)	3.7 (8)	2.1 (9)	
6	$C_4H_5{}^* = C_4H_4 + H$	1.2 (6)	7.4 (6)	4.6 (7)	
		2.0 (4)	2.8 (5)	3.7 (6)	
7	$C_4H_5{}^* + M = C_4H_5 + M$	1.9 (11)	2.3 (11)	2.6 (11)	
8	$C_4H_3{}^d = C_4H_2 + H$	1.3 (−2)	3.3 (2)	6.4 (4)	
		2.0 (−4)	2.0 (1)	6.2 (3)	
9	$C_4H_5 + C_2H_2 = C_6H_7{}^*$	1.9 (7)	5.4 (7)	9.5 (7)	
10	$C_6H_7{}^* = C_6H_6 + H$	6.3 (10)	1.0 (11)	1.6 (11)	
		5.0 (10)	8.3 (10)	1.3 (11)	
11	$C_6H_7{}^* + M = C_6H_7 + M$	2.6 (11)	3.0 (11)	3.5 (11)	
12	$C_2H_3 + C_4H_3 = C_6H_6$	1.6 (11)	1.9 (11)	2.1 (11)	
13	$C_2H_3 + H = C_2H_4$	2.7 (11)	3.1 (11)	3.8 (11)	
14	$C_4H_3 + H = C_4H_4$	2.9 (11)	3.4 (11)	3.8 (11)	
15	$C_4H_3 + C_4H_3 = C_8H_6$	1.3 (11)	1.6 (11)	1.8 (11)	
16	$C_2H_3 + C_2H_3 = C_4H_6$	1.4 (11)	1.6 (11)	1.8 (11)	
17	$C_4H_5{}^* + C_2H_2 = C_4H_4 + C_2H_3$	2.0 (11)	2.3 (11)	3.5 (11)	upper limit
18	$C_2H + C_2H_2 = C_4H_3{}^{*e}$	1.0 (10)	1.0 (10)	1.0 (10)	42
19	$C_4H_3{}^{*e} = C_4H_2 + H$	2.0 (11)	2.3 (11)	2.6 (11)	
20	$C_4H_3{}^{*e} + M = C_4H_3{}^e + M$	2.0 (11)	2.4 (11)	2.7 (11)	
21	$C_2H_2 + C_2H_2 = C_2H + C_2H_3$	1.1 (−15)	2.2 (−7)	6.4 (−3)	
		8.1 (−14)	4.4 (−6)	6.5 (−2)	
22	$C_2H_3 = C_2H_2 + H$	8.7 (−2),[b] 4.9 (−1)[c]	4.5 (2),[b] 2.8 (3)[c]	2.1 (4),[b] 1.3 (5)[c]	
		2.3 (−3),[b] 1.8 (−2)[c]	3.9 (2),[b] 2.2 (3)[c]	3.8 (3),[b] 2.4 (4)[c]	
23	$C_4H_5 + C_4H_5 = C_8H_{10}$	1.0 (11)	1.2 (11)	1.4 (11)	
24	$C_6H_7 + C_6H_7 = C_{12}H_{14}$	1.0 (11)	1.0 (11)	1.0 (11)	
25	$C_2H + C_2H_3 = C_4H_4$	1.0 (11)	1.0 (11)	1.0 (11)	

[a] In M, s units. [b] At 0.1 atm. [c] At 1 atm. [d] Corresponds to the butenyn-2-yl radical. The upper values are estimates from ΔH_f(vinyl) = 70 kcal/mol and the lower ones for ΔH_f(vinyl) = 64 kcal/mol. [e] This radical is the butenyn-1-yl isomer.

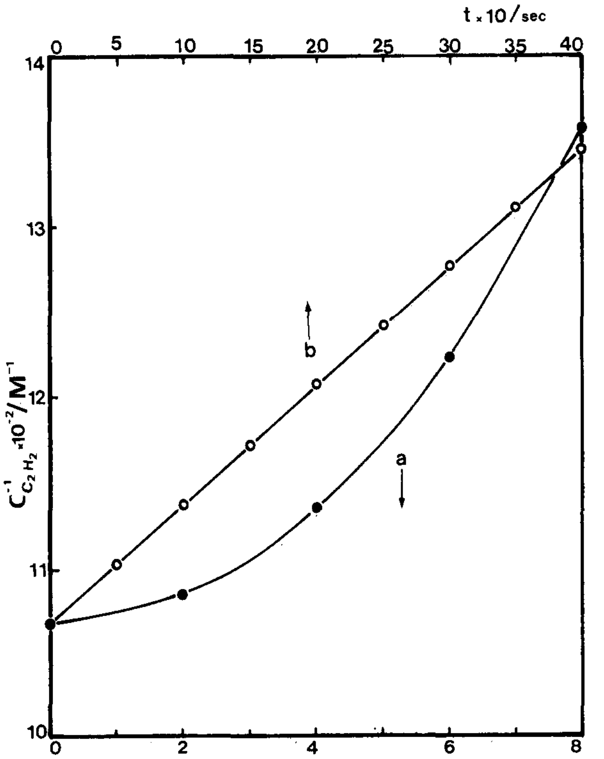


Figure 1. Second-order plots for (a) the Tanzawa and Gardiner mechanism, and (b) mechanism 3b. Experimental conditions: 1300 K; 1 atm of a 1:10 mixture of acetylene in argon.

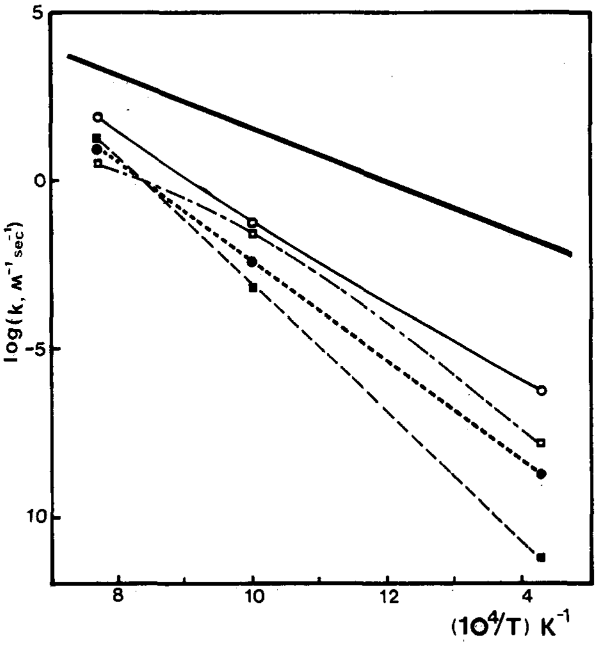


Figure 2. Arrhenius plots of second-order rate constants for acetylene decomposition. Bold line: experimental results, i.e., log k = 10.8 − 41.6/θ. Open circles: mechanism 3b (1 atm). Open squares: mechanism 3a (0.1 atm). Filled circles: mechanism 3a (1 atm). Filled squares: mechanism 2b (1 atm).

Recalling that the estimated activation energy of this reaction is only a lower limit since $E_2 \geq \Delta H_2$, it is clear that mechanism 3a using updated thermochemistry falls short by several orders of magnitude to the observed rates (Figure 2c,d) and hence that free-radical mechanisms are qualitatively and quantitatively inacceptable as realistic descriptions of acetylene pyrolysis. Plausible revision of assumed rate parameters will not suffice to reverse this conclusion. Notice that extending the degree of polymerization beyond benzene might change the products but should not make overall rates any faster as long as reaction 3 remains the slow propagation step. Likely upward changes in the thermochemistry of C_2H_3 and C_2H radicals would only tend to further depress rates.[6,8] However, since rates measured by means of shock-tube techniques can only be shown to be second order with respect to the initial concentration of acetylene[4] and, as noted in the text above, schemes devised to comply with such behavior do not necessarily lead to second-order temporal decay, *free-radical mechanisms are possible at much higher temperatures although they may be different from those just analyzed.*

It might be argued that the preceding analysis and the entire exercise do not bring any progress to the issue since the original question remains unsolved. However, after admitting the failure of radical mechanisms, one is in fact better prepared to seriously consider other possibilities.

The first one, which suggests immediately itself, ascribe the now too fast decomposition rates to a heterogeneous process on account of the inevitable formation of carbon deposits in the course of reaction. However, the early studies by Minkoff et al. in which the surface to volume ratio was varied 200-fold without noticeable effects on rates, together with the remarkable overlap between static, flow, and shock-tube studies about 1200 K, seem to definitely rule out such an explanation.[29]

On the other hand, a concerted four-center dimerization reaction such as the one required to produce vinylacetylene is not only at odds with the characteristic features of the process but also with elementary kinetic predictions. Thus from reported kinetic data on the decomposition of vinyl bromide

$$CH_2{=}CHBr = HC{\equiv}CH + HBr \qquad (26)$$

with $\log A_{26}$ (s^{-1}) = 13.5 at 1000 K and standard entropies we estimate $\log A_{-26}$ ($M^{-1}\ s^{-1}$) = 8.9 for the reverse four-center addition, i.e., about 2 orders of magnitude lower than the A factor of acetylene pyrolysis.[17,30]

We are now in the position to admit that acetylene must be initially converted into an active species, possibly an isomer or an excited state, rather than into free radicals. Since the lowest lying triplet state of acetylene is about 80 kcal/mol above ground state, we advance the notion that such intermediate is actually singlet vinylidene, the carbene isomer of acetylene.[31] More specifically, we propose that the mechanism of acetylene dimerization takes place via

$$C_2H_2 \rightleftharpoons H_2C{=}C: \qquad (27, -27)$$

and

$$H_2C{=}C: + C_2H_2 = C_4H_4 \qquad (28)$$

with $k = 2K_{27}k_{28}$, $\log A = 0.3 + \log A_{28} + \Delta S_{27}°/4.575$, and $E = \Delta H_{27} + E_{28}$, which follow from assuming steady state for $H_2C{=}C$: and recalling that k is pressure independent. Enough theoretical and experimental evidence has been gathered to support this proposal.[32] To begin with, the entropy change $\Delta S_{27}°$ can be accurately calculated from the ab initio geometry and vibrational frequencies of $H_2{=}C$: (and C_2H_2) obtained by Osamura et al.[33] We have actually chosen the set (3149, 3048, 1628, 1250, 760, and 440 cm^{-1}) for $H_2C{=}C$: after scaling the calculated harmonic frequencies by the same factors required to fit the observed ones for C_2H_2.[34] Thus one gets $\Delta S_{27}°$ (1000 K) = 4.45 eu, which in conjunction with $\log A = 10.8$ leads to $A_{28} = 10^{9.5}$ $M^{-1}\ s^{-1}$. This value of the A factor for addition of singlet vinylidene to acetylene comes out to be a factor of 25 smaller than the absolute value of the rate constant for $^1CH_2$ addition to C_2H_2 at 300 K.[36] However, this is reasonable and could have been anticipated since vinylidene carbenes are less electrophilic than methylene and their transition states for addition are expected to be tighter.[37] Again, ab initio calculations fully support the above presumption and, moreover, they suggest the existence of a modest barrier, which we tentatively estimate as $E_{28} = 2$ kcal/mol for the present case.

We now turn to prove that the condition $k_{-27} \gg k_{28}$, which ensures actual equilibration between acetylene and vinylidene prior to addition reactions, really holds under typical experimental conditions. From $E = 41.6$, $E_{28} = 2$, and $E_{-27} = 2.2$ kcal/mol, we get $\Delta H_{27} = 39.6$ kcal/mol and $E_{27} = 41.8$ kcal/mol.[33] The high-pressure A factor of reaction 27 can be directly evaluated from the geometry and vibrational assignments of its transition state as given in ref 33a: A_{27} (1000 K) = $10^{14.4}\ s^{-1}$. The low-pressure rate constants for the same reaction, calculated using eq I at 800 and 1000 K with $\beta_c = 0.5$, lead to the Arrhenius expression: $\log k_{0,27}$ ($M^{-1}\ s^{-1}$) = $13.5 - 38.1/\theta$. Combining the above results a value for the ratio $k_{0,27}[M]/k_{\infty,27} = 0.79[M]$ at 1000 K or 7.9×10^{-4} at $[M] = 10^{-3}$ M is obtained, implying that k_{27} and k_{-27} behave as unimolecular reactions in their second-order region in most experiments. Application of detailed balance immediately yields the desired result: $k_{0,-27} = 10^{-12.1}\ M^{-1}\ s^{-1}$, which is indeed much larger than $k_{28} = 10^{9.1}\ M^{-1}\ s^{-1}$ at 1000 K. These straightforward calculations, which are otherwise free of arbitrary assumptions, confirm in principle the plausibility of our mechanism.

However, as Bauer recently pointed out,[39] standard formulas of unimolecular reaction rate theory such as eq I actually apply to irreversible, exoergic processes and only give upper estimates of actual rate constants for the reverse intramolecular conversions in the low pressure region. This observation is certainly correct in the present case since calculation of $k_{0,-27}$ by means of eq I using direct count estimates of $\rho(E_0)$ for the negligible barrier E_{-27} = 2.2 kcal/mol yields a much lower value than the one previously calculated from the reverse endothermic reaction rate constant $k_{0,27}$ via detailed balance. In fact Osamura's estimate of the vinylidene lifetime for nonactivated isomerization (i.e., for tunneling at zero-point energy) is already so short (~10^{-11} s) that this species should be considered as a region of the C_2H_2 phase space at $E^* = 40$ kcal/mol rapidly explored in the time interval between collisions. The rate of isomerization k_{-27} must then be identified with the rate of collisional deactivation which is in any case almost 2 orders of magnitude larger than k_{28}. This completes our argument. Of course, equilibration could be attained by alternative pathways since its kinetic parameters do not appear in the overall rate constant. Finally we wish to emphasize that justification of the proposed mechanism does not only rest on sound premises but also on experimental evidence.[12,43-45]

Registry No. C_2H_2, 74-86-2; C_4H_4, 689-97-4; C_4H_2, 460-12-8; C_6H_6, 71-43-2; C_2H_4, 74-85-1; $^{\bullet}C_2H$, 2122-48-7; $^{\bullet}C_2H_3$, 2669-89-8; $HC{\equiv}CCH{=}CH^{\bullet}$, 2810-61-9; $CH_2{=}CHCH{=}CH^{\bullet}$, 86181-68-2; $^{\bullet}C_6H_5$, 2396-01-2; $^{\bullet}C_4H$, 53561-65-2; $HC{\equiv}CC^{\bullet}{=}CH_2$, 63707-54-0; $CH_2{=}C$:, 2143-69-3; 2,4-cyclohexadien-1-yl, 12169-67-4.

---

(29) Minkoff, G. J.; Newit, D. M.; Rutledge, P. *J. Appl. Chem.* **1957**, *7*, 406.

(30) Simione, J. M.; Tschuikow-Roux, E. *J. Phys. Chem.* **1970**, *74*, 4075.

(31) Wetmore, R. W.; Schaefer, H. F., III *J. Chem. Phys.* **1978**, *69*, 1648.

(32) (a) Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 982. (b) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. L. *Chem. Phys. Lett.* **1983**, *100*, 124.

(33) (a) Osamura, Y.; Schaefer, H. F., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904. (b) Chen, Y.; Pique, J. P.; Field, R.; Kinsey, J. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987.

(34) *JANAF Thermochemical Tables*, 2nd ed.; U.S. Department of Commerce; NBS: Washington, DC, 1971; NSRDS-NBS 37.

(35) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152.

(36) Böhland, T. Temps, F.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1013, have measured $k = 7.9 \times 10^{10}\ M^{-1}\ s^{-1}$ for $^1CH_2 + C_2H_2$ = products at 300 K.

(37) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(38) For example, whereas the reaction $^1CH_2 + C_2H_4$ does not have a saddle point and the attractive interaction has a range of 3.4 Å (the distance between the carbene carbon atom and the center of the C=C bond), the similar reaction of $^1C(H)OH$ has a well-defined transition state at 1.84 Å. (a) Moreno, M.; Lluch, J. M.; Oliva, A.; Beltran, J. *Chem. Phys.* **1985**, *100*, 33. (b) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770. (c) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.

(39) Bauer, S. H. *Int. J. Chem. Kinet.* **1985**, *17*, 367.

(40) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(41) Paddon-Row, M. N.; Pople, J. A. *J. Phys. Chem.* **1985**, *89*, 2768.

(42) Lange, W.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 165.

(43) Ghibaudi, E.; Colussi, A. J. *J. Phys. Chem.*, in press.

(44) Durán, R. P.; Amorebieta, V. T.; Colussi, A. J., submitted for publication in *Int. J. Chem. Kinet.*

(45) Kiefer, J. H., personal communication.