3714 J. Phys. Chem. **1985**, *89*, 3714–3725

Figure 10, which includes the detailed rate equations, is in the supplementary material.

The rate constants used here for reactions M1–M4 are derived from Table I. Because reversibility is ignored, they are effectively too large. The Tyson[5] "low" rate constants are expected to give better agreement with experiment for such things as the amplitude of the oscillations and the fraction of Ce(III) oxidized to Ce(IV) in each cycle. The shift from process A to process B will be too slow using the "low" rate constants.

Experimental Section

Oxalic acid, acetone, and sulfuric acid were Baker Analyzed Reagent grade. The NaBr, $KBrO_3$, and $Ce(SO_4)_2$ used were MCB Reagent grade and $Ce_2(SO_4)_3$ was Aldrich Reagent grade. All chemicals were used without further purification except $KBrO_3$ which to remove Br^- was slurried several times in methanol and dried at 150 °C before use.[46] The water used was singly distilled from a Corning AG-3 still. Most experiments were carried out with solutions deoxygenated by purging with N_2 for at least 15 min, although spot checks showed no detectable kinetic effects of dissolved oxygen.

Reactions were run in a 10-mm, teflon-stoppered quartz cuvette located in the sample compartment of a Beckman Model 24 UV–visible spectrophotometer. Reagents were brought to 29 °C by a Braun 1420 thermostatted water circulator before introduction to the cuvette, which was maintained at 29 ± 0.1 °C. For rapid reactions the cuvette was placed in the closed spectrophotometer and the reactants were introduced through tubes by means of a pair of syringes. Mixing occurred in a chamber placed before the cuvette. The resulting digital data were entered into the University of Montana DEC-2060 computer.

Experiments on the complete oscillatory system were carried out with stirring and monitored potentiometrically with a Photovolt platinum electrode, an Altex double-junction reference electrode with KNO_3 in the outer jacket, and an Orion Model 701A digital meter. Output was to a Bausch and Lomb potentiometric recorder.

Simulations were carried out using the DEC-2060 computer with a Tektronix Model 4001 graphics terminal and the Gear numerical integration package.[47] Experimental data and the corresponding simulation were displayed on the same axis, and appropriate rate constants were adjusted to give the best agreement between experimental data and simulation. Hard copies were obtained from a Houston Instruments DP-11 digital plotter. A general discussion of methods of simulating oscillating reactions has been given by Edelson and Rabitz.[48]

Acknowledgment. This work was partially supported by the National Science Foundation under Grant CHE80-23755 and benefited from discussions with Professors Maria Burger and Endre Körös of the L. Eötvös University, Budapest and Professor John J. Tyson of the Virginia Polytechnic Institute and State University. We thank the University of Montana Computer Center for computing facilities and Mr. Robert Yokelson for programming help.

Registry No. BrO_3^-, 15541-45-4; Br^-, 24959-67-9; Br_2, 7726-95-6; Ce, 7440-45-1; oxalic acid, 144-62-7; acetone, 67-64-1.

Supplementary Material Available: Programs to integrate the full model and the Br_2-hydrolysis-controlled Oregonator and plots of log [$HBrO_2$], log [Ce(IV)], log [Br_2], log [HOBr], and [Ce(IV)] vs. time for the Br_2-hydrolysis-controlled Oregonator (18 pages). Ordering information is available on any current masthead page.

---

(46) Field, R. J.; Raghavan, N. V.; Brummer, J. G. *J. Phys. Chem.* **1982**, *86*, 2443.

(47) Hindmarsh, A. C. "Gear: Ordinary Differential Equation Solver", Technical Report No. UCID-3001, Rev. 2, Lawrence Livermore Laboratory, 1972; Based upon Gear, C. W. *Commun. ACM* **1971**, *14*, 185.

(48) Edelson, D.; Rabitz, H. In "Oscillations and Traveling Waves in Chemical Systems", Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985; Chapter 6.

High-Temperature Stabilities of Hydrocarbons

S. E. Stein* and A. Fahr[†]

Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899 *(Received: February 19, 1985)*

A chemical thermodynamic analysis of hydrocarbon molecules from 1500 to 3000 K is presented for species $C_{2n}H_{2m}$, $n = 1$–21, $m = 1$–8. With group additivity as the primary estimation method, the nature and chemical thermodynamic properties of the most stable molecules ("stabilomers") are found. Concentrations of these molecules are then examined in equilibrium with acetylene and molecular hydrogen after taking into account numbers of isomers. Thermodynamically favored pathways leading to large, condensed polyaromatic species are examined in detail. Two general types of paths are found. At higher H_2/C_2H_2 ratios ($\gtrsim 1$), most species on these paths are polycyclic aromatic molecules and, depending on partial pressures of C_2H_2 and H_2, a free energy barrier appears in the range 1400–1800 K which increases sharply with increasing temperature. At lower H_2/C_2H_2 ratios, many smaller species are acyclic, and as this ratio becomes smaller the barrier declines and becomes less sensitive to temperature. A brief discussion of the connection between these results and the kinetics of carbon polymerization is then presented.

Introduction

At sufficiently high temperatures, hydrocarbons "polymerize" to form complex mixtures of polyaromatic molecules, polyacetylenes, and solid carbon. Because of the practical importance and ubiquity of these processes, they have long been the subject of study. Chemical complexities and analysis problems have, however, prevented the development of widely accepted chemical mechanisms for these reactions, even in relatively well-controlled reaction environments such as those generated in shock-heated gases.

In this work we present a chemical thermodynamic analysis of hydrocarbons intended to aid the development of such mechanisms. A global equilibrium analysis is presented here which can both place constraints on reaction paths and provide a logical framework on which mechanisms may be built. In addition, the

---

[†] Guest worker from Chemistry Department, Georgetown University, Washington, DC 20057.

0022-3654/85/2089-3714$01.50/0 © 1985 American Chemical Society

set of thermodynamic properties derived for this analysis may be useful in the development of detailed kinetic models.

Of perhaps more fundamental interest, we examine the question of thermodynamic stability at elevated temperatures. "Intuition" concerning stability based on room temperature experience can fail drastically at high temperatures. Polyacetylenes, for instance, while explosively unstable at room temperature, are more stable than paraffins at high temperatures. The present analysis will assist in the development of "intuition" at elevated temperatures, where entropy plays a critical role in determining molecular stability.

In a previous analysis we examined benzenoid polynuclear aromatic molecules in equilibrium with acetylene and molecular hydrogen.[1] Under typical conditions, polymerization along a hypothetical path involving only these species was found to pass through a free energy barrier above ~1700 K. That is, along the polymerization pathway from acetylene to graphite stabilities of the intermediate polyaromatic molecules first decrease and then increase. The least stable species is "positioned" at this barrier. The magnitude of this barrier (i.e., the inverse of the equilibrium concentration of species at the barrier) increased with increasing temperature and hydrogen density and with decreasing acetylene density. We hypothesized that in certain reaction environments this thermodynamic barrier might create a kinetic barrier for soot formation and that the position of this barrier might provide a basis for the definition of a soot "nucleus".

The present work broadens this analysis to include other classes of stable hydrocarbons, to account for numbers of isomers and to examine this barrier in more detail. In the course of this extension, structures of the most stable hydrocarbons in the range 1500–2500 K are deduced.

The present study is carried out in the following stages:

(a) The scope is defined.

(b) Methods for estimating thermodynamic properties are discussed along with the influence of errors on the present calculations.

(c) For each atomic formula of interest, structures and properties of the most stable individual molecules ("stabilomers"[2]) and classes of molecules are discussed and compared with less stable classes.

(d) Equilibria are examined as a function of atomic formula, temperature, and partial pressures of acetylene and molecular hydrogen.

(e) A brief discussion of the relation between these equilibria and the kinetics of carbon polymerization is presented.

Scope

This analysis examines thermodynamically stable hydrocarbons C_2H_2 to $C_{42}H_{16}$ in the range 1500–3000 K. Below 1500 K, there exists no thermodynamic barrier toward the growth of polyaromatic hydrocarbons,[1] so that carbon polymerization is likely to be controlled entirely by kinetic factors. Godleski et al.[2] found that adamantane ($C_{10}H_{16}$) and related sp^3 diamondlike molecules are the most stable large hydrocarbons at 298 K. Above 1000 K, however, Gibbs energies of formation of these compounds are far greater than those of polyaromatic molecules containing comparable numbers of C atoms.

At temperatures above 3000 K polyaromatic hydrocarbon molecules are so unstable that they are not likely to serve as intermediates in carbon formation.

For a given number of C atoms, molecules containing more than a critical number of H atoms are not examined. Along any series of hydrocarbons—$C_{2n}H_2$, $C_{2n}H_4$, $C_{2n}H_6$, ...—once this number of H atoms is exceeded, high-temperature thermodynamic stabilities of the most stable isomers drastically decline. This effect, examined in detail later, occurs when further addition of H atoms cannot increase the maximum number of polyaromatic carbon atoms in the molecule.

Since molecules containing odd numbers of C atoms cannot be completely conjugated and possess relatively high H/C ratios, they are generally less stable than molecules of comparable structure containing even numbers of C atoms. Therefore, only the latter are considered in this work.

Since only closed-shell hydrocarbons are quantitatively examined in this work, only species with even numbers of H atoms are considered. It is important to note, however, that the most thermodynamically stable free radicals at high temperatures generally have odd numbers of both H and C atoms[3] (methyl, CH_3; propargyl, C_3H_3; benzyl, C_7H_7; perinaphthenyl, $C_{13}H_9$). Their properties therefore do not precisely follow the trends of the molecules examined in this work.

Ionized species are not examined in this work. Stabilities of selected polyaraomtic cations of interest in flames was the subject of a recent study.[4]

Stabilities of $C_{2n}H_{2m}$ are discussed in terms of their hypothetical equilibrium concentrations in reaction 1. This approach is used

$$nC_2H_2 \rightleftarrows C_{2n}H_{2m} + (n - m)H_2 \qquad (1)$$

since the predominant gases in high-temperature hydrocarbon equilibria are acetylene and hydrogen.[3] Moreover, in many actual reactions, as in the afterburning region of a fuel-rich flame, acetylene and hydrogen are the major non-oxygen-containing molecules.

A more commonly used approach for examining complex equilibria in which total densities of carbon and hydrogen atoms are fixed[3,5] is not suitable for the present analysis. Because of the stability of large polyaromatic molecules, if this approach were used, computed equilibrium concentrations of all species would depend on the choice of molecules included in the calculation.

Equilibria involving solid graphite or very large two-dimensional layers of graphite are also not examined since in these cases concentrations of most gas-phase hydrocarbons of interest become vanishingly small. Equilibria of small hydrocarbons have already been thoroughly examined in the presence and absence of graphite by Bauer and co-workers[3] and, more recently, in the presence of graphite and a large graphitelike molecule by Lee and Palmer.[6]

Estimation Methods

The primary estimation method used in this analysis is "group additivity".[7] In this method, the value for a thermodynamic property of a molecule is estimated by summing the contributions from each of the structural groups that compose the molecule. In a hydrocarbon molecule, each group is associated with one carbon atom. After summing group values, the desired molecular property is corrected for non-nearest-neighbor effects not accounted for by groups (the rotational symmetry number, σ, for instance, lowers the entropy by $R \ln \sigma$). Groups and group values used in this work are listed in Table I and discussed in the Appendix. All equilibrium calculations were done by computer using a least-squares, fourth-order polynomial fit to the heat capacities. This form was used in order to be compatible with existing equilibrium code.[5]

In cases where different isomers of benzenoid polyaromatic hydrocarbons exist, we have chosen as most stable the one with the largest number of Kĕkule structures. The reliability of this simple method is well documented in the literature.[8] When

---

[1] Stein, S. E. *J. Phys. Chem.* **1978**, *82*, 566.

[2] Godleski, S. A.; Schleyer, P. v. R.; Osawa, E.; Wipke, W. T. *Prog. Phys. Org. Chem.* **1981**, *13*, 63.

[3] (a) Cowperswaite, A. M.; Bauer, S. H. *J. Chem. Phys.* **1962**, *36*, 1743. (b) Duff, R. E.; Bauer, S. H. *Ibid.* **1962**, *36*, 1754.

[4] Stein, S. E. *Combust. Flame* **1983**, *51*, 537.

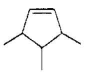
[5] Gordon, S.; McBride, B. J. "Computer Program for Calculation of Complex Chemical Equilibria Composition"; NASA Lewis Laboratories: Cleveland, OH, 1976; NASA SP-273.

[6] Lee, C. W. M.S. Thesis, The Pennsylvania State University, University Park, PA, August 1983 (work done under the supervision of H. B. Palmer).

[7] (a) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (b) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

[8] (a) Swinborne-Sheldrake, R.; Herndon, W. C. *Tetrahedron Lett.* **1975**, *10*, 755. (b) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404.

TABLE I: Groups and Group Additivity Values[a] Used in This Work

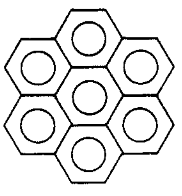
group[x]	$\Delta H°_{298}$/kJ·mol^{-1}	$S°_{298}$/ J·mol^{-1}·K^{-1}	$C°_{p,T}$/J·mol^{-1}·K^{-1} 300	400	500	600	800	1000	1250	1500	2000	2500	3000
C_B–(H)	13.8	48.2	13.8	18.8	23.1	26.6	31.6	35.1	38.2	40.3	42.8	44.2	45.0
C_B–(C_B)	20.7	-36.1	12.9[r]	16.6	19.2	21.2	23.6	25.1	26.1	26.8	27.4	27.8	27.9
C_B–(C_d)	23.8	-32.6	14.0[s]	15.3	16.9	18.8	21.3	23.2	24.8	25.8	26.8	27.3	27.6
C_B–(C_t)	23.8	-46.6[l] (-32.6)[f]	14.0[t]	15.3	16.9	18.6	21.3	23.2	24.8	25.8	26.8	27.3	27.6
C_d–$(H)_2$	26.2	115.5	21.5	26.6	31.2	35.4	41.9	47.0	51.6	55.0	59.2	61.5	62.9
C_d–(C_B)(H)	28.4	26.7	18.6[u]	24.2	28.2	31.2	35.3	38.1	40.5	42.2	44.3	45.5	46.1
C_d–(C_d)(H)	28.4	26.7	18.6[v]	24.2	28.2	31.2	35.3	38.1	40.5	42.2	44.3	45.5	46.1
C_d–(C_t)(H)	28.4	33.6[m] (26.7)[f]	18.6[u]	24.2	28.2	31.2	35.3	38.1	40.5	42.2	44.3	45.5	46.1
C_t–(H)	112.7	103.3	22.1	25.2	27.4	29.0	31.6	33.8	35.9	37.5	39.7	40.9	41.6
C_t–(C_d)	118.0[e] (122.2)[f]	26.9	11.0[m]	12.7	14.3	15.7	18.0	19.7	21.2	22.1	23.2	23.7	24.0
C_t–(C_B)	103.2[g] (122.2)[f]	26.9	11.0[l]	16.1	19.0	20.6	22.3	23.1	23.6	23.9	24.4	24.6	24.8
C_t–(C_t)[b]	107.1[h]	24.6[n]	14.8[n]	17.0	18.4	19.4	20.9	21.9	22.8	23.3	24.0	24.3	24.5
C_{FR}–(C_{FR})$(C_B)_2$	20.1	-20.9	12.6	15.4	17.5	19.3	22.0	23.7	25.0	25.8	26.6	27.0	27.2
C_{FR}–$(C_{FR})_2$(C_B)	15.5	-20.9	12.6	15.4	17.5	19.3	22.0	23.7	25.0	25.8	26.6	27.0	27.2
C_{FR}–$(C_{FR})_3$	6.1	7.6	8.4[w]	13.0	16.3	18.5	21.1	22.4	23.2	23.7	24.2	24.5	24.6
C_{tB}[b]	207.8[i]	47.6[o]	10.0[o]	11.7	13.1	14.4	16.1	17.3	18.3	19.1	20.2	20.9	21.3
C_B–(·)[c]	258.1[j]	43.2[p]	10.8[p]	12.9	14.8	16.2	18.1	19.3	20.2	20.8	21.3	21.6	21.7
 [d]	107.1[k]	25.7[q]	24.1[q]	30.0	34.3	37.4	41.8	44.0	45.9	47.2	48.4	48.9	49.1

[a] Except where noted, $\Delta H_f°_{298}$ and $S°_{298}$ were taken from ref 7 and $C°_{p,T}$ were derived from vibrational frequencies for the simplest molecules containing these groups given by: Shimanouchi, T. *Natl. Stand. Ref. Data. Ser.*, *Natl. Bur. Stand.* **1972**, No. 39. [b] Values for this group have not been published before. [c] Values for the radical center in a phenyl radical. [d] Acenaphthylene ring group.[18] Derived from the difference between values for acenaphthylene and naphthalene. [e] From heat of hydrogenation measurements.[16] [f] Literature value.[7] [g] From heat of hydrogenation measurements for ethynylbenzene,[28] diphenylacetylene,[16b,28,29] and diphenyl-1,3-butadiyne.[29] A value of 109.3 kJ was used in the present calculations; see text for discussion. [h] See text for discussion. [i] From average of two published values.[14] [j] Assumes C–H bond dissociation energy in benzene of 462 kJ mol^{-1}.[7] [k] From difference in ΔH_f for acenaphthylene and naphthalene.[18] [l] From average of ethynylbenzene and diethynylbenzene values.[30] [m] From frequencies in reference.[27] [n] Average of diacetylene[20] and triacetylene values.[21] [o] From frequencies given in ref 31. [p] Obtained by deleting three frequencies from benzene (3100, 1500, 1200 cm^{-1}). [q] Reference 18. [r] From frequencies for biphenyl given by: Raton, J. E.; Lippincott, E. R. *Spectrochim Acta* **1959**, *15*, 627. [s] Using frequencies estimated by authors for styrene and adjusting hindered rotational barrier to match C_p values in ref 24. [t] Set equal to values for [C_B–(C_d)]. [u] Set equal to values for [C_d–(C_d)(H)]. [v] Used frequencies for 1,3-butadiene (see reference in note *a*) along with hindered rotor values adjusted to match C_p values in ref 24. [w] From pyrene frequencies.[32] [x] Benson-group notation is used.[7] See ref 10 for a brief explanation.

needed, differences between resonance energies of two isomers are approximated by the formula 110(kJ mol^{-1}) ln (ratio of numbers of Kĕkule structures).[8]

It is important to note that the *absolute* accuracy of estimated equilibrium concentrations is very poor for large molecules and worsens with increasing size. This is a result of the fact that errors in thermodynamic quantities, like the quantities themselves, are additive functions of molecular groups. To illustrate this point, consider a hypothetical hydrocarbon molecule composed of n identical groups, each with an uncertainty in $\Delta H_f°$ of ±1500 J mol^{-1} (4.184 J = 1 cal) and in $S°$ of ± 1.0 J mol^{-1} K^{-1}. Assuming that $\Delta C_p = 0$, the error in equilibrium concentration of this molecule at, say 1500 K, is $\exp\{1500n/R1500) + 1.0n/R\} = \exp(2.0n/R)$. The uncertainty in equilibrium concentrations of a molecule for which, say, $n = 30$, is a factor of 1400. Clearly, equilibrium constants and concentrations of this nature can be highly inaccurate.

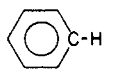
On the other hand, if the thermodynamic stability of a molecule is thought of as the *temperature* at which its equilibrium concentration (or constant) reaches a *specified value*, errors are far less severe and do not necessarily grow with increasing molecular size. In this case, it is the fractional error rather than the absolute error in thermodynamic properties that is significant. To illustrate this point, assume that the above hypothetical molecule is formed in reaction 1 with a reaction enthalpy of 100n kJ mol^{-1} and a reaction entropy of $-50n$ J mol^{-1} K^{-1} (this is roughly the case for coronene, $C_{24}H_{12}$



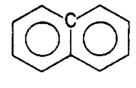
In this case, regardless of molecular size, the fractional error in the temperature at which the equilibrium constant reaches a specified value is 0.035 (=(1.5/100) + (1.0/50)). For instance, this equilibrium constant is unity at 1500 ± 50 K. For this reason, because relative errors for molecules of similar size and structure tend to cancel and because properties of very large, condensed polyaromatics are forced to converge to those of an isolated layer of graphite by our estimation technique,[1] it is possible to discuss relative stabilities of large molecules with reasonable confidence even in the presence of large absolute errors in individual thermodynamic properties. Uncertainties in the equilibrium concentrations reported in this work are therefore best viewed as uncertainties in the temperature and/or concentrations of H_2 and C_2H_2. Generally speaking, we expect such uncertainties in temperature to be less than 100 K and uncertainties in concentrations to be less than a factor of 2.

Structures and Properties of Thermodynamically Stable Molecules

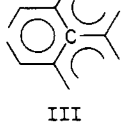
For most atomic formulas of interest, a number of different distributions of functional groups are possible. Each distribution corresponds to a "class" of molecules consisting of members that are structural isomers of each other.[9] The major varieties of carbon atoms used for defining these classes are acetylenic, olefinic, benzene-like (I), benzenoid fused-ring (II), graphitic (III), and



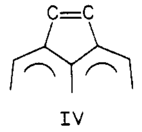
I



II



III



IV

---

(9) Alberty, R. A. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 1318.

acenaphthylene-ring (IV). Some of these varieties correspond to more than one Benson-type group,[7,10] so that a single class as defined in the present work may contain isomers having different sets of such groups.

The stability of a class of molecules depends on the number of isomers in that class as well as the symmetry number of each isomer. These factors contribute an amount $\sum_{i=1}^{I}(1/\sigma_i)$ to the equilibrium concentration of a class, where I is the total number of geometrical and optical isomers and σ_i is the rotational symmetry number of the ith isomer.

The intrinsic entropy[11] of each isomer in a class is assumed to be the same as for the isomer with the greatest intrinsic entropy as calculated by group additivity. The ΔH_f value assigned to a class is set equal to the lowest ΔH_f value for any member of the class. In view of uncertainties in group values, a more detailed analysis in which the dispersion of thermodynamic properties is accounted for has not been attempted.

Structures of the most stable isomers within the most stable classes at the nominal temperature of 1500 K are given for molecules $C_{2n}H_{2m}$ in an $n \times m$ grid in Figure 1. In Table II are given numbers of isomers, I, as well as the above isomer correction factor for each of these classes.

Structures of the most stable isomers are deduced on the basis of (1) rotational symmetry, (2) steric effects, (3) group values, and (4) stability of the polyaromatic cluster. The identity of the most stable isomer is often less certain than the identity of the most stable class.

A discussion of the most stable $C_{2n}H_{2m}$ classes, most of which are represented in Figure 1, will now be presented. This discussion is given in terms of logical series. In each series the number of C atoms varies while the number of H atoms is fixed.

$C_{2n}H_0$. This series is not represented in Figure 1 because of the extreme instability and uncertain thermochemistry of the smallest members and the unknown structures and energies of larger members. We can, however, make some general statements about this series.

To illustrate the instability of small C_{2n} species, at 1800 K and in the presence of 1 atm of H_2, equilibrium concentrations of C_2 and C_4 are estimated[12] to be a factor of 10^{11} and 10^{10} times smaller than C_2H_2 and C_4H_2, respectively.

Since all valence electrons in single-ring (cyclic polyacetylene) C_{2n} molecules are involved in covalent bonding, these molecules may be far more stable than linear C_{2n} species, since the latter contain nonbonding electrons. This difference in stability is expected to be particularly large for C_{2n} molecules large enough for their cyclic forms to be relatively unstrained.

While theoretical studies[13] indicate that polycyclic C_4 and C_6 species may be more stable than linear or monocyclic isomers, quantitative accuracy is questionable and different theories can yield very different results.

Since solid carbon (graphite or diamond) + H_2 is more stable than any hydrocarbon molecule at high temperature[1,3,6] as C_{2n} species grow in size, their highly condensed isomers must eventually also become more stable than any hydrocarbon molecule. Interior carbon atoms of these species may be either graphitelike (sp^2) or diamondlike (sp^3). Carbon atoms at the periphery are expected to be very unstable due to strain and/or unpaired valence

TABLE II: Numbers of Stable Isomers (Upper Entry) and Isomer Correction Factors (Lower Entry; = $\sum 1/\sigma_i$) for the Most Stable Classes of $C_{2n}H_{2m}$ Molecules

Number of Hydrogen Atoms	Number of Carbon Atoms 2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5	1 0.5										
4	1 0.25	1 1	2 2.5	5 5	11 8.75	19 14	23 20.5	30 30	45 41.25	55 55	74 71										
6	1 0.06	1 0.5	1 0.08	1 0.5	4 1.75	7 4.63	16 10.5	26 21	50 38.25	65 58.5											
8		4 2.5	3 1.5	1 0.5	1 0.25	1 0.5	1 0.25	2 2	12 9	30 30	90 83										
10				4 1.75	6 4.5	1 0.25	2 0.75	1 .25	1 1	2 2	1 1	1 0.25	3 2.5	18 14	68 65						
12								2 1	4 1.8	3 1.75	2 1	1 .04	1 0.5	3 1.25	3 1.66	3 1.25	1 0.5	1 0.5	1 1	12 10.5	29 28.17
14											12 8	12 9.04	9 7.75	8 5.25	3 1.75	1 0.5	2 2	9 6.5	10 10	15 12.5	5 5
16																110 37	44 25.25	31 36	17 15.25	10 8.5	3 1.75

---

(10) Each of these groups is associated with a carbon atom and is defined in terms of its covalently bound neighboring atoms (given in parentheses). Five types of carbon atoms are distinguished: (1) saturated, C; (2) double-bonded, C_d; (3) triple-bonded, C_t; (4) aromatic (benzene-like), C_B; (5) fused-ring (part of two or three aromatic rings), C_{FR}. By convention, covalently bound atoms always associated with a carbon atom type are not explicitly noted (e.g., C_d is always attached to a second C_d). To illustrate, vinylnaphthalene (1- or 2-) contains the following groups: 7 [C_B–(H)], 2 [C_{FR}–(C_{FR})(C_B)$_2$], 1 [C_B–(C_d)], 1 [C_d–(C_B)(H)], 1 [C_d–(H)$_2$].

(11) $S_{\text{intrinsic}} = S_{\text{actual}} + R \ln(\sigma/n)$, where σ is the rotational symmetry number and n is the number of optical isomers. $S_{\text{intrinsic}}$ is the part of S that is "additive".

(12) "JANAF Thermochemical Tables", 2nd ed.; *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.* **1971**, No. 37.

(13) (a) Slanina, Z.; Zahradnik, R. *J. Phys. Chem.* **1977**, *81*, 2252. (b) Whitesides, R. A.; Krishnan, R.; Defrees, D. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *78*, 538.

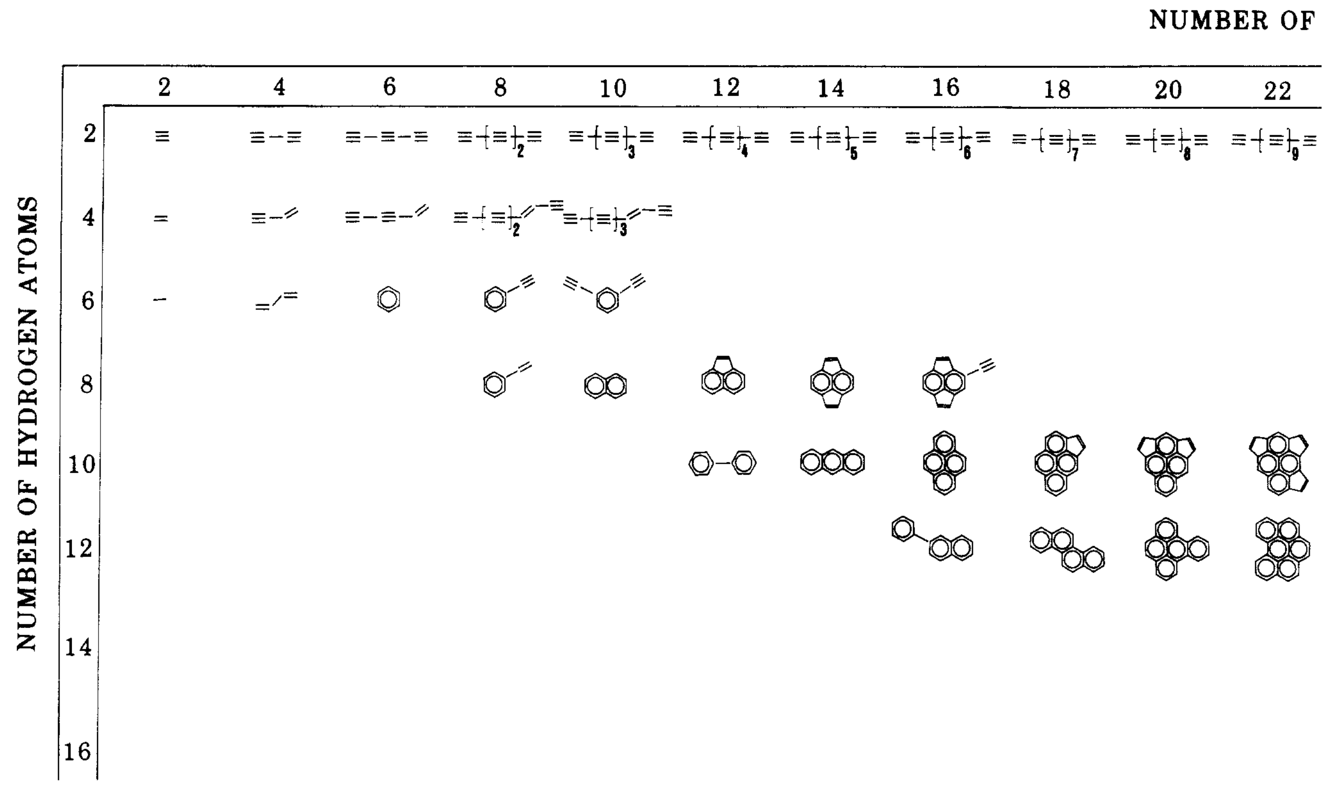
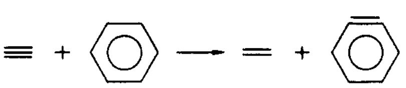


Figure 1. Structures of the most stable isomers in the most stable classes of $C_{2n}H_{2m}$ molecules ("stabilomers"[2]).

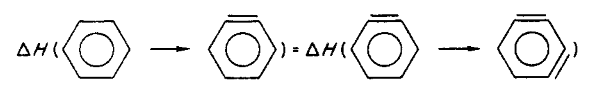
electrons. Since graphitelike molecules (polyaromatics) have both significantly lower ratios of edge to interior C atoms and lower Gibbs energies per C atom than diamondlike molecules (polyadamantanes) of comparable C number, the former molecules should always be more stable than the latter at high temperatures. However, the relative contribution of edge atoms to overall thermodynamic stability will decrease with increasing size.

$C_{2n}H_2$. The most stable classes of moderately sized $C_{2n}H_2$ molecules are expected to be the polyacetylenes. These are the simplest classes of molecules examined; only one polyacetylene isomer exists for each atomic formula. Each of these molecules is linear and has a symmetry number of two.

The next most stable class of $C_{2n}H_2$ molecules are single-ring species containing one double bond and $n - 1$ triple bonds. From the group tables, one finds that if there were no strain in these molecules, their heats of formation would be ~170 kJ mol^{-1} lower than those of the polyacetylenes. However, due to their strain energy and to their relatively low entropy, unless n is very large these cyclic molecules are predicted to be distinctly less stable than polyacetylenes. The magnitude of this strain energy is evident from the 210 ± 40 kJ mol^{-1} endothermicity of the reaction[14]

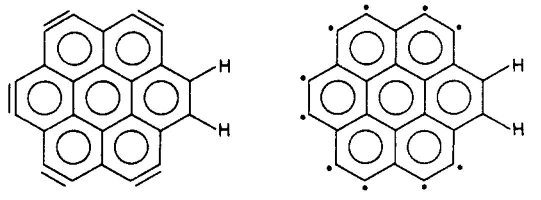


Assuming that



the isomerization of triacetylene to cyclohexene-3,5-diyne is estimated to be 220 ± 80 kJ mol^{-1} endothermic. Moreover, on the basis of known trends in strain energy[15] it could be argued that the strain introduced by the second triple bond is substantially greater than that introduced by the first. This cyclization is further disfavored by a sizable entropy loss of ~-60 kJ mol^{-1} K^{-1} (Table I).

Very large, highly condensed polyaromatic $C_{2n}H_2$ species, like the large C_{2n} molecules mentioned in the previous section, are expected to become increasingly stable with increasing size. Although any discussion of such species must be speculative, their general properties can be coarsely estimated by assigning unstable group values to their "exterior" carbon atoms and "graphitelike" group values to their "interior" atoms and then comparing their Gibbs energies to those of polyacetylenes with the same atomic formula. We assume that each polyaromatic $C_{2n}H_2$ species may be derived from a benzenoid polyaromatic $C_{2n}H_{2m}$ molecule by replacement of $2m - 2$ benzene groups, [C_B-(H)], with the same number of unstable edge groups. In an effort to bracket the stability of the latter groups, calculations were done for two edge-atom types. The more stable edge group was assigned properties of a triply bonded C atom in benzyne [C_{tB}], and the less stable edge group was assigned properties of the radical-centered C atom in the phenyl radical [C_B-(·)]. For example, the hypothetical $C_{24}H_2$ species containing these two edge types have the structures

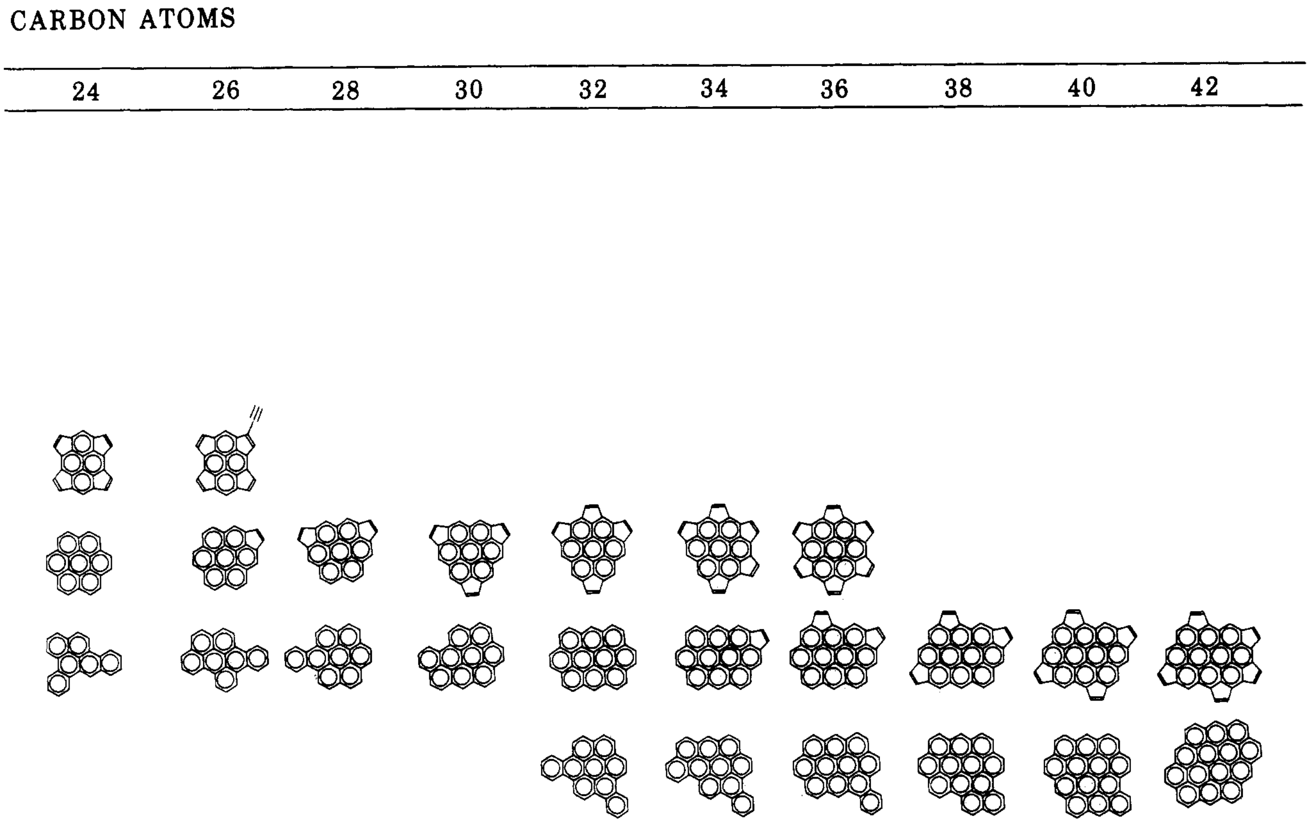


Calculations predict that sufficiently large polybenzenoid $C_{2n}H_2$ species are more stable than polyacetylene $C_{2n}H_2$ molecules below some temperature, T^*, and are less stable above this temperature. For the more stable edges (benzyne-type) results are (T^* is in parentheses) $C_{24}H_2$ (1000 K); $C_{34}H_2$ (1600 K); $C_{42}H_2$ (2100 K); $C_{54}H_2$ (2400 K); $C_{96}H_2$ (3100 K). For the less stable edge types (polyradicals), results are $C_{24}H_2$ (the polyacetylene form is always more stable); $C_{34}H_2$ (300 K); $C_{42}H_2$ (1200 K); $C_{54}H_2$ (1800 K);

---

[14] (a) Pollack, S. K.; Hehre, W. J. *Tetrahedron Lett.* **1980**, *21*, 2483. (b) Rosenstock, H. M.; Stockbauer, R.; Parr, A. C. *J. Chim. Phys.* **1980**, *77*, 745.

[15] (a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. (b) Liebman, J. F. In "Molecular Structures and Energetics", Vol. III, Greenberg, A., Liebman, J. F., Eds.; VCH Publishers: Deerfield Beach, FL, in press.



$C_{96}H_2$ (2800 K). Clearly, in the temperature range of interest in this work, n must be quite large before graphitelike molecules become more stable than polyacetylenes. On the other hand, regardless of approximations for stabilities of edge C atoms, polyaromatic molecules larger than $C_{54}H_2$ are certain to be more stable than polyacetylenes up to at least 1800 K.

$C_{2n}H_4$. The most stable $C_{2n}H_4$ molecules are acyclic and contain one double bond and $n - 1$ triple bonds. Symmetry numbers of molecules with $n > 1$ are unity except for an occasional twofold symmetric molecule. Available data indicate that cis and trans isomers are equally stable,[16] in contrast to geometrical isomers of olefins.[17] No information is available on thermodynamic effects of branching in polyalkenynes so that branched and unbranched isomers are assumed to be equally stable. Heats of hydrogenation[16] indicate that isomers with a terminal vinyl group are somewhat more stable (~10 kJ mol^{-1}) than isomers with terminal acetylenic groups. However, uncertainties in relative Gibbs energies are comparable to this difference.

The next most stable class contains a single benzyne (*o*-phenylene) ring, and $n - 3$ acetylenic bonds. 1-Hexene-3,5-diyne is predicted to be as stable as benzyne at ~600 K, and at 1800 K it is predicted to be 200 times more stable.

All other classes of cyclic $C_{2n}H_4$ molecules examined appear to be far less stable than the above two classes.

$C_{2n}H_6$. Below ~2700 K, the most stable $C_{2n}H_6$ molecules with $n \geq 3$ contain one benzene ring and $n - 3$ triple bonds.

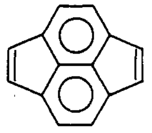
Not until temperatures above ~3100 K are reached do individual acyclic isomers become more stable than aromatic molecules. At 1800 K, benzene is ~5000 times as stable as 1,3-hexadiene-5-yne and ethynylbenzene is ~7000 times as stable as 1,3-octadiene-5,7-diyne.

The fact that acyclic $C_{2n}H_6$ molecules have more geometrical isomers than do aromatic $C_{2n}H_6$ molecules means that the former class becomes more stable than the latter at a temperature lower than the crossover temperature for individual members of these two classes. We estimate that such aromatic and acyclic classes have the same stability near 2700 K, or 400 K lower than the point of equal stability for individual molecules.

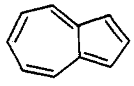
In view of its estimated 120 kJ mol^{-1} higher heat of formation (ignoring any antiaromaticity) and its lower entropy, benzocyclobutadiene is always far less stable than ethynylbenzene. The same argument applies to 1,3,5-cyclooctatriene-7-yne, whose ΔH_f is ~170 kJ mol^{-1} greater than that of ethynylbenzene even assuming no ring strain.

$C_{2n}H_8$. The most stable molecules $C_{2n}H_8$, $n \geq 5$, contain one naphthalene moiety, up to two acenaphthylene-type rings, and $n - 7$ triple bonds.

As a result of their significantly lower ΔH_f (110 kJ mol^{-1}) and only slightly lower entropy (~20 J mol^{-1} K^{-1}), acenaphthylene rings are more stable than acetylene substituents up to 3000 K. At 1800 K, for instance, acenaphthylene and "diacenaphthylene" (V) are estimated to be 40 times and 800 times more stable than 1-naphthylacetylene and 1-naphthyldiacetylene. However, classes containing the latter molecules have more isomers than those containing the former. Thus the temperature at which these two classes are equally stable is about 2500 K.


V

Azulene (VI) has a comparable entropy and a 160 kJ mol^{-1} higher ΔH_f than its isomer naphthalene,[17] and hence can never be as stable.

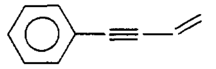

VI

As in the case of benzene, ring-opened naphthalene isomers do not become more stable than aromatic molecules until very high temperatures are reached. For instance, naphthalene is more stable than any isomeric substituted benzene, e.g.

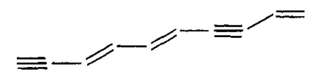
---

(16) (a) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404. (b) Flitcroft, T. L.; Skinner, H. A. *Trans. Faraday Soc.* **1958**, *54*, 47.

(17) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

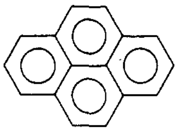


below ~3000 K, and is more stable than any totally acyclic species, e.g.



below ~3200 K. Isomerism lowers the temperatures at which these classes are equally stable by 300–500 K. We find that these general conclusions apply to all polycyclic structures; polycyclic classes are more stable than ring-opened classes up to at least 2500 K.

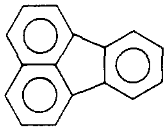
$C_{2n}H_{10}$. The most stable classes of these molecules below ~2500 K with $n \geq 8$ contain one pyrene unit (VII) and up to



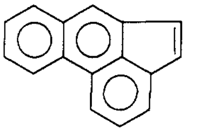
VII

four acenaphthenylene units and have any remaining C atoms in acetylenic groups.

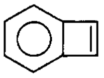
Other classes of $C_{2n}H_{10}$ molecules with different but much less stable aromatic nuclei exist, such as VIII and IX. Their heats



VIII



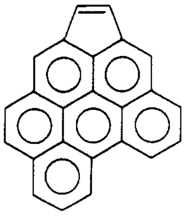
IX

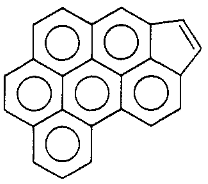


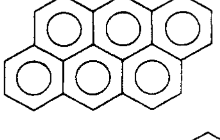
X

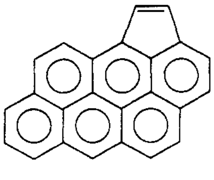
of formation are greater than pyrene by 64 and 90 kJ mol^{-1},[17,18] respectively.

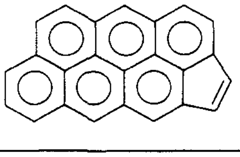
$C_{2n}H_{12}$, $C_{2n}H_{14}$, $C_{2n}H_{16}$. The most stable isomers of these molecules were obtained by using the principles discussed above. In all cases we find that the classes represented in Figure 1 are the most stable up to at least 2000 K, and often to 2500 K. It is noteworthy that this even holds for classes containing only one member of high symmetry. In the case of $C_{24}H_{12}$, for instance, the most stable class contains a single member, coronene, which has a symmetry number of 12. Even though the next most stable class contains five species











each with a symmetry number of 1, this class is less stable than coronene up to ~2000 K.

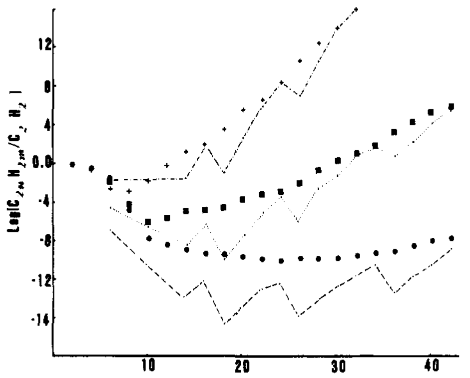


Figure 2. Concentrations of $C_{2n}H_{2m}$ classes in equilibrium with C_2H_2 and H_2 along the most favorable polymerization path for $P_{C_2H_2} = 0.03$ atm, $P_{H_2} = 0.10$ atm, and $T/K = 1600$ (+), 1900 (■), and 2200 (●). Broken lines are concentrations of classes of benzenoid polyaromatic under similar conditions.

Equilibria

Relative equilibrium concentrations of the most stable classes of $C_{2n}H_{2m}$ molecules represented in Figure 1 are given in Table IIIa–f in the form of $n \times m$ grids over a range of temperature and partial pressures of C_2H_2 and H_2. These concentrations are nearly equal to estimated total $C_{2n}H_{2m}$ concentrations since, as discussed above, other classes are unimportant below ~2000 K. Above this temperature the relative increase in stability of the other classes with increasing temperature is small in comparison to the drastic decline in stability of all classes of hydrocarbons containing more hydrogen than the polyacetylenes.

Concentrations of classes on the most thermodynamically favorable paths leading from C_2H_2 to very large, stable molecules are given in boldface in Table IIIa–f. Polymerization along these paths occurs by a logical series of single-step processes, each involving addition of H_2 (vertical steps), addition of C_2H_2 (diagonal steps) or addition of C_2H_2 and loss of H_2 (horizontal steps).

A close inspection of these grids shows that under many conditions, any polymerization path leading to stable molecules must pass over a thermodynamic barrier. In such cases, paths shown in Table IIIa–f are directed through the lowest barriers possible. The class positioned at this barrier will be denoted $C_{2n}H_{2m}^*$.

Our earlier studies,[1] examined a polymerization pathway involving only individual, unsubstituted benzenoid polyaromatic molecules. As seen in Table IIIa–f with reference to Figure 1, many classes on the present polymerization paths are not such molecules, so there is not an exact correspondence between the present and previous paths.

On the other hand, as long as $H_2/C_2H_2 > 1$, the classes on the present most stable polymerization paths are not vastly different in structure or stability than purely benzenoid molecules with comparable C numbers. This is illustrated in Figure 2 where relative concentrations of both of these classes are plotted vs. C number.

This correspondence, however, seriously breaks down when H_2/C_2H_2 ratios are less than unity. Under these conditions, the classes of smaller molecules in the present paths are composed primarily of polyacetylenes. These paths allow polymerization to, in effect, bypass relatively unstable classes of small polycyclic molecules and to thereby pass through lower thermodynamic barriers. This situation is illustrated in Table IIIf, where $H_2/C_2H_2 = {}^1/_3$.

To examine more closely the magnitude of these free energy barriers, concentrations of $C_{2n}H_{2m}^*$ are shown as a function of acetylene and molecular hydrogen concentration in Figure 3a–c. These plots illustrate the dramatic increase in the magnitude of the barrier with increasing temperature when $H_2/C_2H_2 \gtrsim 1$. As H_2/C_2H_2 declines, the temperature sensitivity and magnitude of this barrier also declines and ultimately disappears.

---

(18) Stein, S. E.; Barton, B. D. *Thermochim. Acta* **1981**, *44*, 265.

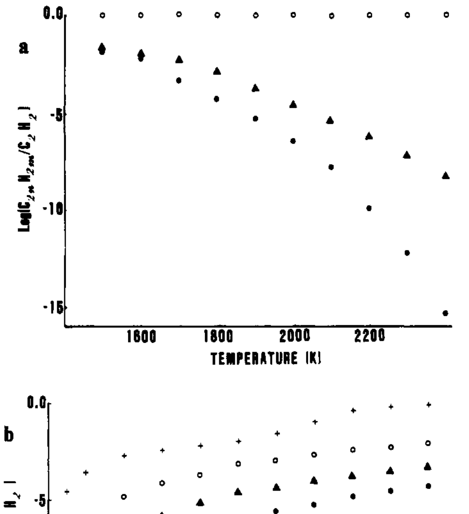


Figure 3. Concentrations of the least stable classes ($C_{2n}H_{2n}$*) in equilibrium with C_2H_2 and H_2 along the most thermodynamically favored polymerization pathway as a function of (a) temperature, (b) acetylene pressure, and (c) hydrogen pressure. (a) $P_{C_2H_2} = 0.10$ atm and $P_{H_2} = 0.02$ (○), 0.10 (▲), 0.50 atm (●). (b) $P_{H_2} = 0.10$ atm and $T = 1600$ (+), 1800 (○), 2000 (▲), 2200 K (●). (c) $P_{C_2H_2} = 0.10$ atm and $T = 1600$ (▲), 1800 (○), 2000 (+), 2200 K (●).

To explore the relation between the magnitude of this barrier and partial pressures of acetylene and hydrogen, in Table IV the temperatures at which concentrations of $C_{2n}H_{2m}$* reach 10^{-2} and 10^{-4} of the acetylene concentration are shown for a range of partial pressures. This dependence can be very strong. For instance, the temperature where $C_{2n}H_{2m}$*$/C_2H_2$ is 10^{-4} is only 1500–1600 K when $P_{C_2H_2} = 0.01$ atm and $P_{H_2} = 0.10$ atm, but moves up to 1900–2000 K when $P_{C_2H_2}$ is increased by factor of 10.

In order to justify our neglect of species with high H/C ratios and to examine the relation between the C/H ratio of a class and its stability, relative concentrations for the series $C_{24}H_{2m}$, $m = 1$–8, are plotted in Figure 4 under selected conditions. Clearly, classes with $m > 6$ are always far less stable than coronene ($m = 6$) at high temperatures. Also, the greater entropy and number of isomers of classes for which $m < 6$ do not compensate for their inherently low stability, except at very low H_2/C_2H_2 ratios or very high temperatures.

Kinetic Implications

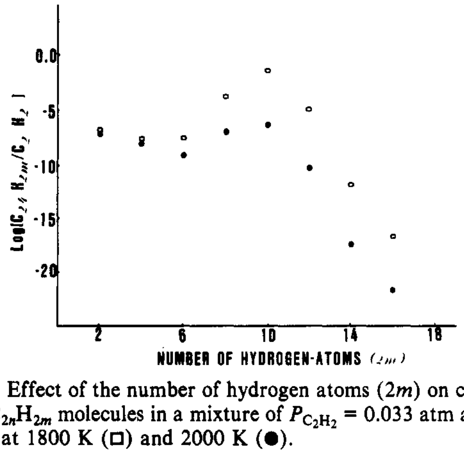


Figure 4. Effect of the number of hydrogen atoms ($2m$) on concentrations of $C_{2n}H_{2m}$ molecules in a mixture of $P_{C_2H_2} = 0.033$ atm and $P_{H_2} = 0.10$ atm at 1800 K (□) and 2000 K (●).

The thermodynamic barrier discussed above can, in effect, create a kinetic barrier for polymerization reactions involving polyaromatic intermediates. A closely related idea, that of a "ceiling temperature" above which polymerization rates decline, is commonly used in the analysis of conventional polymerization kinetics.

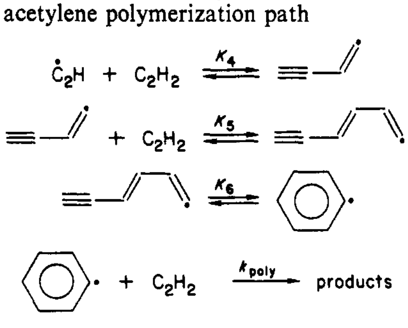
From a mechanistic viewpoint, this barrier is a consequence of the "reversibility" of those polymerization steps that reduce numbers of species as illustrated by the following idealized polymerization sequence

$$I + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IM \qquad (2)$$

$$IM + M \xrightarrow{k_3} \text{products} \qquad (3)$$

If the reversibility of this path, R, is expressed as the rate of reaction of I in the absence of reversibility, $k_2[I][M]$, relative to the actual steady-state rate, $k_2k_3[I][M]^2/(k_{-2} + k_3[M])$, then $R = 1 + k_{-2}/(k_3[M])$. Since k_2 and k_3 are often of the same magnitude, it is useful to define $\alpha \equiv k_2/k_3$, so that $R = 1 + \alpha(K_2[M])^{-1}$ where K_2 is the equilibrium constant for reaction 2. Note that the term $K_2[M]$ is equal to the equilibrium concentration of IM relative to I, a value closely related to relative equilibrium concentrations calculated in this work. Due to the generally large magnitude of the enthalpy and entropy change for reaction 2, the temperature dependence of R is determined primarily by the contribution from K_2. The temperature at which the reversibility factor is equal to 2 (or, $k_{-2} = k_3[M]$) may be viewed as the ceiling temperature for this reaction.

To illustrate this sort of analysis, consider the following hypothetical acetylene polymerization path



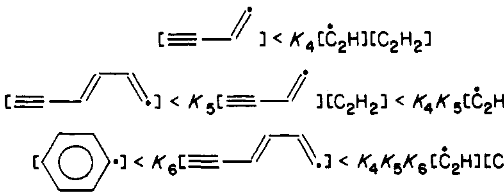
(4)

(5)

(6)

(7)

and assume that these are the only paths leading to the formation of the intermediates shown. In this case, the following set of inequalities hold



Therefore, the actual rate of polymerization

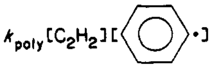


TABLE III: Log Equilibrium Concentrations of $C_{2n}H_m$ Classes Relative to C_2H_2[a]

Number of Carbon Atoms

Number of Hydrogen Atoms	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	**-.7**	-1.4	-2.2	-2.9	-3.6	-4.3	-5.0	-5.7	-6.5	-7.9	-7.9	-8.6	-9.3	-10.1	-10.8	-11.5	-12.2	-12.9	-13.6	-14.4
4	1.8	**-2.5**	-2.8	-3.2	-3.7	-4.2	-4.8	-5.3	-5.9	-6.5	-7.1										
6	-4.9	-5.2	**-2.0**	**-3.0**	-3.2	-3.5	-3.5	-3.9	-4.3	-4.8	-5.3										
8					**-2.3**	**-.7**	**.2**	.4	.3	.1	.1										
10						-4.4	-2.5	**.5**	**2.3**	**3.9**	**4.8**	5.4	5.7	5.8							
12								-4.6	-2.2	1.1	4.1	**6.2**	**8.3**	**9.9**	**11.3**	12.4	13.2	13.7	14.1	14.4	14.0
14											-2.2	1.3	4.6	7.8	10.6	**13.0**	**15.1**	**16.9**	**18.3**	19.7	20.5
16															5.0	8.3	11.5	14.5	17.5	**20.1**	**22.5**

a

	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	**-.7**	**-1.5**	-2.2	-2.9	-3.6	-4.4	-5.1	-5.8	-6.6	-7.3	-8.0	-8.7	-9.5	-10,2	-10.9	-11.6	-12.4	-13.1	-13.8	-14.6
4	-2.4	-3.0	-3.4	**-3.8**	-4.3	-4.8	-5.4	-5.9	-6.5	-7.1	-7.7										
6	-5.9	-6.4	-3.9	-4.9	**-5.1**	-5.4	-5.8	-6.2	-6.7	-7.2											
8					-5.4	**-4.2**	**-3.6**	**-3.5**	-3.5	-3.7	-4.0										
10						-8.2	-6.9	-4.6	**-3.1**	**-1.9**	**-1.3**	**-1.0**	-.7	-.7							
12								-9.6	-7.8	-5.2	-2.8	-1.3	**.4**	**1.6**	**2.7**	**3.4**	3.9	4.0	4.4	4.7	4.3
14											-9.1	-6.2	-3.5	-1.0	1.1	2.9	**4.7**	**6.1**	**7.2**	**8.2**	**8.6**
16															-4.5	-1.8	.8	3.2	5.5	7.5	**9.2**

b

	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	**-.7**	**-1.5**	**-2.2**	-2.9	-3.7	-4.4	-5.1	-5.9	-6.6	-7.3	-8.1	-8.8	-9.6	-10.1	-11.0	-11.8	-12.5	-13.2	-14.0	-14.7
4	-2.9	-3.5	-3.8	-4.2	**-4.7**	**-5.3**	-5.8	-6.4	-7.0	-7.6	-8.2										
6	-6.8	-7.3	-5.5	-6.4	-6.6	**-6.9**	-7.3	-7.7	-8.2	-8.8											
8					-7.9	-7.0	**-6.7**	**-6.6**	**-6.6**	-6.9	-7.2										
10						-11.2	-10.4	-8.6	-7.4	**-6.5**	**-6.2**	**-6.2**	**-5.9**	-5.9							
12								-13.6	-12.3	-10.2	-8.4	-7.4	-6.0	**-5.0**	**-4.3**	**-3.8**	**-3.6**	-3.8	-3.4	-3.1	-3.6
14											-14.6	-12.2	-10.0	-8.0	-6.5	-5.2	-3.7	**-2.6**	**-1.8**	**-1.1**	-.9
16															-12.0	-9.9	-7.8	-5.9	-4.1	-2.7	**-1.5**

c

TABLE III (Continued)

	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	- **.7**	-1.5	-2.2	-2.9	- 3.6	- 4.4	-5.1	- 5.8	- 6.6	- 7.3	- 8.0	- 8.7	- 9.5	-10.2	-10.9	-11.7	-12.4	-13.1	-13.8	-14.6
4	-1.9	-2.5	**-2.8**	-3.3	-3.8	- 4.3	- 4.8	-5.4	- 6.0	- 6.6	- 7.2										
6	-4.9	-5.3	-2.9	**-3.9**	-4.1	- 4.4	- 4.7	-5.2	- 5.6	- 6.2											
8					**-3.9**	- **2.7**	- **2.1**	**-1.9**	- 2.0	- 2.2	- 2.5										
10						- 6.1	- 4.8	-2.5	- **1.0**	**.2**	**.8**	1.1	1.4	1.4							
12								-7.0	- 5.2	- 2.6	.2	**1.3**	**3.6**	**4.3**	**5.3**	6.0	6.5	6.6	7.0	7.3	6.9
14											6.0	- 3.1	- .4	2.1	4.3	**6.0**	**7.8**	**9.2**	**10.3**	**11.3**	11.8
16															- .8	1.9	4.5	6.9	9.2	11.1	**12.9**

d

	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	- **.3**	- **.5**	- **.8**	-1.0	- 1.3	-1.5	-1.8	-2.0	-2.3	-2.5	-2.8	-3.0	-3.3	-3.5	- 3.8	- 4.0	- 4.3	- 4.5	- 4.8	- 5.0
4	-2.4	-2.6	-2.4	-2.4	**-2.4**	- 2.4	-2.5	-2.6	-2.7	-2.8	-3.0										
6	-5.9	-5.9	-2.9	-3.5	-3.2	- **3.0**	-2.9	-2.9	-2.9	-2.9											
8					-3.5	- 1.8	- **.7**	- **.1**	.3	.6	.8										
10						- 5.8	-4.0	-1.2	**.8**	**2.4**	**3.5**	**4.3**	5.0	5.5							
12								-6.2	-4.0	- .9	1.9	3.9	**6.1**	**7.9**	**9.3**	10.6	11.6	12.1	13.0	13.7	13.8
14											-4.3	-1.0	2.2	5.2	7.8	**10.1**	**12.3**	**14.2**	**15.8**	**17.2**	18.2
16															2.2	5.4	8.5	11.3	14.1	16.5	**18.8**

e

	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
2	**0.0**	**.2**	**.5**	**.7**	**.9**	**1.1**	**1.4**	**1.6**	1.8	2.0	2.3	2.5	2.7	3.0	3.2	3.4	3.6	3.9	4.1	4.3	4.5
4	-2.9	-2.6	-1.9	-1.4	- .9	- .5	- .1	.3	**.7**	1.0	1.3										
6	-6.9	-6.4	-2.9	-3.0	-2.2	-1.6	-1.0	- .5	0.0	**.4**											
8					-3.0	- .9	.7	1.8	2.7	3.4	**4.1**										
10						-5.3	3.0	.2	2.7	4.8	6.4	**7.6**	**8.8**	**9.8**							
12								-5.3	-2.5	1.0	4.3	6.8	**9.4**	**11.7**	**13.6**	**15.4**	**16.8**	**17.9**	19.2	20.4	21.0
14											-2.4	1.4	5.1	8.6	11.6	14.3	17.1	19.4	**21.5**	**23.4**	24.9
16															5.6	9.2	12.8	16.1	19.4	22.3	**25.0**

f

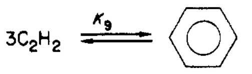
[a] For $P_{C_2H_2}$/atm = 0.10 and P_{H_2}/atm = 0.30 at T/K = (a) 1700, (b) 1900, and (c) 2100, and at T/K = 1900 for $P_{C_2H_2}$/atm = 0.30 and (d) P_{H_2}/atm = 1.0 atm, (e) P_{H_2}/atm = 0.30, and (f) P_{H_2}/atm = 0.1. Classes on the most stable pathways are denoted by boldface values.

TABLE IV: Temperatures at Which the Equilibrium Concentrations of Least Stable Classes ($C_{2n}H_{2m}$*) Become Equal to 10^{-2} and 10^{-4} of C_2H_2 Concentration, for a Range of $P_{C_2H_2}$ and P_{H_2}

$P_{C_2H_2}$/ atm	P_{H_2}/ atm	$[C_{2n}H_{2m}^*]/[C_2H_2] = 10^{-2}$		$[C_{2n}H_{2m}^*]/[C_2H_2] = 10^{-4}$	
		T/K	$C_{2n}H_{2m}^*$	T/K	$C_{2n}H_{2m}^*$
0.001	0.001	1208	$C_{12}H_4$	1540	$C_{16}H_6$
0.001	0.003	1149	C_4H_4	1453	C_8H_6
0.001	0.01	1149	C_4H_4	1418	C_8H_6
0.01	0.01	1380	$C_{10}H_4$	1710	$C_{18}H_6$
0.01	0.03	1320	C_4H_4	1606	C_8H_6
0.01	0.1	1319	C_4H_4	1563	C_8H_6
0.1	0.1	1618	$C_{10}H_4$	1923	$C_{18}H_6$
0.1	0.3	1550	C_4H_4	1796	C_8H_6
0.1	1.0	1550	C_4H_4	1742	C_8H_6

can be no greater than $k_{poly}[C_2H_2]\{K_4K_5K_6[\dot{C}_2H][C_2H_2]^2\}$. Making use of the equilibrium constants for reactions 8 and 9 one may

(8)



(9)

write, $K_9 = K_4K_5K_6K_8$, hence the lower limit for R may be written

$$R \geq \frac{k_4K_8}{k_{poly}}\left(\frac{1}{K_9[C_2H_2]^2}\right) \qquad (10)$$

where k_4 is the forward rate constant for reaction 4. The term k_4K_8/k_{poly} is, in effect, a kinetic factor accounting for the relative efficiency of reactions 4 and 7 corrected for thermochemical differences. Its value is estimated to be of the order 0.1 at 1800 K and to have relatively little temperature dependence. The inverse of the term in parentheses in expression 10 is equal to the hypothetical equilibrium concentration of benzene relative to acetylene ($K_9[C_2H_2]^3/[C_2H_2]$) and is the overwhelming factor determining the magnitude of this expression. The net rate of reaction sequence 4–7 will therefore slow down when $K_9[C_2H_2]^2$ becomes less than ~0.1. This occurs near 1600 K when $P_{C_2H_2} = 0.1$ atm and is 200 K higher when $P_{C_2H_2} = 1$ atm. Above these temperatures, rates will diminish in parallel with K_9 ($K_9 \propto \exp\{-72000/T\}$).

With appropriate modifications, the above analysis can be expanded to include any polymerizing nuclei and any mechanism. In a mechanism in which the only species involved are C_2H_2, H_2, and these nuclei, the analysis is particularly simple; the concentration of each nucleus cannot be greater than its hypothetical equilibrium concentration. We are now in the process of applying these ideas to a wider range of reactions.

Summary

(1) A self-consistent set of group values from 300 to 3000 K is given for estimating thermodynamic properties of stable $C_{2n}H_{2m}$ hydrocarbons.

(2) A set of isomer corrections for these molecules has been compiled.

(3) Structures of the most stable classes of $C_{2n}H_{2m}$ species at high temperatures are determined.

(4) Relative stabilities of the most stable classes of hydrocarbons are examined as a function of temperature and acetylene and hydrogen concentration.

(5) A thermodynamic barrier toward carbon polymerization is examined which accounts for all possible $C_{2n}H_{2m}$ species.

(6) The relationship between the above thermodynamic barrier and possible kinetic barriers is discussed.

Acknowledgment. This work was supported in part by a grant from NASA-Lewis Laboratories. Helpful discussions with Wing Tsang and Joel Liebman are gratefully acknowledged. We also thank Prof. D. W. Rodgers for a preprint of his recent work.[29]

Appendix

Chemical Thermodynamic Group Values.[10] Although most group values used in this work (Table I) were similar to published values,[1,7,18,19] in some cases substantial differences exist. The basis for our choices of new values, along with values for several new groups, are discussed below.

All heat capacity values were derived in this work so that calculations could be done up to 3000 K. The harmonic oscillator–rigid rotator approximation was used for all of these calculations in order to maximize cancellation of errors due to anharmonicity in computed equilibrium constants.

All values for groups involving triply bonded carbon, C_t, were rederived in this work since some values were not available ($[C_t-(C_t)]$) and others were based on old or roughly estimated thermodynamic data.

S°_{298} and $C^\circ_{p,T}$ values for the $[C_t-(C_t)]$ group were obtained from vibrational assignments for diacetylene[20] and triacetylene.[21] Its $\Delta H_f{}^\circ_{298}$ value was taken as the average of values derived in two different ways from the literature heat of hydrogenation of (conjugated) 5,7-dodecadiyne in solution.[22] The first method obtained the gas-phase heat of hydrogenation by assuming that the heat of vaporization of this diyne is 3 ± 2 kJ mol^{-1} greater than dodecane. This difference is based on gas chromatographic retention time data for related substances.[23] In the second method, differences in heats of hydrogenation of 5,7-dodecadiyne and (nonconjugated) 3,8-dodecadiyne gave $\Delta H_f[C_t-(C_t)] - \Delta H_f[C_t-(C)] = -8.2$ kJ mol^{-1}, assuming the same heats of vaporization for these two substances. The well-established value for $\Delta H_f[C_t-(C)] = 115$ kJ mol^{-1} [7] was then used to obtain the desired value. The resulting estimate for $\Delta H_f{}^\circ_{298}$ of diacetylene is 440 kJ mol^{-1}, which is significantly lower than published values of 470,[24] 471,[3] and 456[25] kJ mol^{-1}. The origin of the first of these values is uncertain, but the latter two were derived from the hydrogenation data that we use but in different ways.

The present set of values for $[C_t-(C_t)]$ yields an equilibrium constant for reaction 11 of $K_{11} = 0.39\exp(780/T)$ over the range

$$C_2H_2 + C_{2n}H_2 \rightleftarrows C_{2n+2}H_2 + H_2 \qquad (11)$$

1500–2500 K. This is a factor of 2.5 greater than the value estimated from presumed polyacetylene equilibria in premixed flames.[25,26] If it is desired to match this flame-derived equilibrium constant, we suggest using a value of $\Delta H_f[C_t-(C_t)] = 114$ kJ mol^{-1}, which is 7 kJ mol^{-1} greater than the value given in Table I.

Values for $[C_t-(C_d)]$ and $[C_d-(C_t)]$ were rederived from available data[16,27] and do not differ greatly from previous values. Values for the $[C_t-(C_B)]$ and $[C_B-(C_t)]$ groups were based on averages of heat of hydrogenation measurements[29] and vibrational assignments for phenylacetylene and related compounds.[30] Since

---

(19) Stein, S. E.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 314.

(20) Hardwick, J. L.; Ramsay, D. A.; Gornean, J. M.; Lavighe, J.; Cabana, A. *J. Mol. Spectrosc.* **1979**, *76*, 492.

(21) Bjarnor, E.; Christensen, D. H.; Nielsen, O. F.; Augdahl, E.; Kloster-Jensen, E.; Rogstad, A. *Spectrochim. Acta, Part A* **1974**, *30A*, 1255.

(22) Flitcroft, T.; Skinner, H. A.; Whiting, M. C. *Trans. Faraday Soc.* **1957**, *53*, 784.

(23) (a) Welsch, T.; Engewald, W.; Berger, P. *Chromatographia* **1978**, *11*, 5. (b) Rang, S.; Kuningas, K.; Orav, A.; Eisen, O. *J. Chromatogr.* **1976**, *119*, 451.

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

(25) Bittner, J. D. Ph.D. Thesis, Massachusetts Institute of Technology, Boston, MA, 1981.

(26) Bonne, W.; Homann, K. H.; Wagner, H. Gg. *Symp. (Int.) Combust., [Proc.] 10, 1964*, **1965**, 503.

(27) Torneng, E.; Nielsen, C. J.; Klaeboe, P.; Hopf, H.; Priebe, H. *Spectrochim. Acta, Part A* **1980**, *36A*, 975.

(28) (a) Rodgers, D. W.; McLafferty, F. W. *Tetrahedron* **1971**, *27*, 3765. (b) Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395.

(29) Davis, H. E.; Allinger, N. L.; Rodgers, D. W., manuscript in preparation.

(30) (a) King, A. W.; So, S. P. *J. Mol. Spectrosc.* **1970**, *36*, 468. (b) Evans, J. C.; Nyquist, R. A. *Spectrochim. Acta* **1960**, *16*, 918. (c) Danchinov, K. M.; Rodionov, A. N.; Gastilovitch, E. A.; Shigorin, D. N. *Opt. Spectrosc.* **1971**, *31*, 341. (d) King, G. W.; van Putten, A. A. G. *J. Mol. Spectrosc.* **1978**, *70*, 53.

vibrational assignments were used to obtain certain group values that were previously estimated by analogy to related groups, there are some sizable differences between the present and previous $S°_{298}$ and $C°_{p,T}$ group values.

The value of $\Delta H_f[C_t-(C_B)]$ used in our calculations was 109.2 kJ mol^{-1} based on the average of values derived from ref 26b and 28. However, as this paper was nearing completion, we became aware of recent, as yet unpublished heat of hydrogenation data in hexane for compounds containing this group by D. W. Rodgers et al.[29] New data were given for phenylacetylene (−277 ± 2 kJ mol^{-1}), diphenylacetylene (−249 ± 3 kJ mol^{-1}), and diphenyl-1,3-butadiyne (−496 ± 4 kJ mol^{-1}). These data can be fit very well if the above group value is lowere by 6 kJ mol^{-1} to 103.2 kJ mol^{-1} and an old value for phenylacetylene[28b] is discarded. We recommend use of this new value in future calculations. If we had used this new value, equilibrium concentrations of molecules containing these groups would be increased by somewhere between 60% (at 1500 K) and 27% (at 3000 K) per group. This would not have a serious effect on our calculations.

Values for a triply bonded C atom in benzyne, $[C_{tB}]$, were derived for the first time from available data.[14,31]

Values of C_p for the $[C_{FR}-(C_{FR})_3]$ group were derived from pyrene frequencies[32] rather than from graphite[19] in order to eliminate anharmonicity effects.

Registry No. H_2, 1333-74-0; C_2H_2, 74-86-2; C_2H_4, 74-85-1; C_2H_6, 74-84-0; C_4H_2, 460-12-8; C_4H_4, 689-97-4; C_4H_6, 106-99-0; C_6H_2, 2235-12-3; C_6H_4, 7023-69-0; C_6H_6, 71-43-2; C_8H_2, 6165-96-4; C_8H_4, 51615-63-5; C_8H_6, 536-74-3; C_8H_8, 100-42-5; $C_{10}H_2$, 32597-32-3; $C_{10}H_4$, 96915-01-4; $C_{10}H_6$, 1785-61-1; $C_{10}H_8$ (naphthalene), 91-20-3; $C_{12}H_2$, 32597-33-4; $C_{12}H_8$, 208-96-8; $C_{12}H_{10}$, 92-52-4; $C_{14}H_2$, 38646-98-9; $C_{14}H_8$, 187-78-0; $C_{14}H_{10}$, 120-12-7; $C_{16}H_2$, 38646-95-6; $C_{16}H_8$, 96915-03-6; $C_{16}H_{10}$ (pyrene), 129-00-0; $C_{16}H_{12}$, 612-94-2; $C_{18}H_{10}$, 27208-37-3; $C_{18}H_{12}$, 218-01-9; $C_{20}H_2$, 36060-68-1; $C_{20}H_{10}$, 96915-04-7; $C_{20}H_{12}$, 192-97-2; $C_{22}H_2$, 96915-02-5; $C_{22}H_{10}$, 96915-05-8; $C_{22}H_{12}$, 191-24-2; $C_{24}H_{10}$, 96915-06-9; $C_{24}H_{12}$ (coronene), 191-07-1; $C_{24}H_{14}$, 192-65-4; $C_{26}H_{10}$, 96915-07-0; $C_{26}H_{12}$, 92627-26-4; $C_{26}H_{14}$, 190-95-4; $C_{28}H_{12}$, 96915-08-1; $C_{28}H_{14}$, 190-70-5; $C_{30}H_{12}$, 96928-77-7; $C_{30}H_{14}$, 6596-38-9; $C_{32}H_{12}$, 96915-09-2; $C_{32}H_{14}$, 190-26-1; $C_{32}H_{16}$, 190-66-9; $C_{34}H_{12}$, 96915-10-5; $C_{34}H_{14}$, 96915-11-6; $C_{34}H_{16}$, 75449-99-9; $C_{36}H_{12}$, 96928-78-8; $C_{36}H_{14}$, 96915-12-7; $C_{36}H_{16}$, 75449-88-6; $C_{38}H_{14}$, 96915-13-8; $C_{38}H_{16}$, 91374-35-5; $C_{40}H_{14}$, 96915-14-9; $C_{40}H_{16}$, 94417-26-2; $C_{42}H_{14}$, 96915-15-0; $C_{42}H_{16}$, 77968-44-6; $C_{16}H_{10}$ (isomer 1), 206-44-0; $C_{16}H_{10}$ (isomer 2), 201-06-9; $C_{24}H_{12}$ (isomer 1), 96915-18-3; $C_{24}H_{12}$ (isomer 2), 190-88-5; $C_{24}H_{12}$ (isomer 3), 96915-19-4; $C_{24}H_{12}$ (isomer 4), 96915-20-7; $C_{24}H_{12}$ (isomer 5), 96915-21-8; carbon, 7440-44-0; azulene, 275-51-4; 1-phenyl-3-butene-1-yne, 13633-26-6; 3,5,9-decatriene-8-diyne, 96915-16-1; 1-hexene-3,5-diyne, 7023-69-0; benzyne, 462-80-6; 1,3-hexadiene-5-yne, 10420-90-3; 1,3-octadiene-5,7-diyne, 96915-17-2; benzocyclobutadiene, 4026-23-7; 1,3,5-cyclooctatriene-7-yne, 4514-69-6; polyacetylene, 25067-58-7.

---

(31) Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *J. Mol. Struct.* **1979**, *51*, 275.

(32) Nelander, B.; Sunner, S. *J. Chem. Phys.* **1966**, *44*, 2476.

FTIR Study of the Kinetics and Mechanism for the Cl-Atom-Initiated Reactions of $SiHCl_3$

H. Niki,* P. D. Maker, C. M. Savage, L. P. Breitenbach, and M. D. Hurley

Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (Received: February 19, 1985)

On the basis of FTIR product analysis of the UV–visible (λ ≥ 300 nm) photolysis of Cl_2–$SiHCl_3$ mixtures in 700 torr of N_2-O_2, Cl atoms were shown to predominantly undergo an H-atom abstraction reaction rather than an attachment/displacement reaction with $SiHCl_3$. The corresponding rate constant $k[Cl + SiHCl_3]$ was determined at 298 K to be 2.9 × 10^{-11} cm^3 molecule^{-1} s^{-1} by the competitive kinetic method with reference to the Cl + C_2H_6 reaction. IR absorption bands attributable to two new gaseous products, $SiCl_3OCl$ and $SiCl_3OH$, were detected in the subsequent oxidation of the primary radical $SiCl_3$. Kinetic and spectroscopic evidence was also obtained for the NO_2-addition reaction of the oxy and peroxy radicals $SiCl_3O$ and $SiCl_3OO$. A plausible mechanism for the formation of these products is presented.

Introduction

While the gas-phase oxidation of small alkyl radicals at ca. 300 K has been the subject of extensive studies,[1] relatively little is known about the corresponding reaction of their silicon analogues, i.e., silyl radicals. Recently, the oxidation of SiH_3 radicals has been examined in this laboratory[2] by the FTIR spectroscopic detection method combined with the photochemical generation of the SiH_3 radicals via $Cl_2 + h\nu(\lambda \geq 300\text{ nm}) \rightarrow 2Cl$ followed by $Cl + SiH_4 \rightarrow SiH_3 + HCl$. Evidence has been obtained for the rapid isomerization/dissociation of the peroxy adduct SiH_3OO to yield $HSi({=}O)OH + H$. In contrast, the CH_3OO produced in the $CH_3 + O_2$ reaction is thermochemically stable and the analogous dissociation channel to form $HC({=}O)OH + H$ is not operative.[3-6]

In the present FTIR study, the UV–visible (λ ≥ 300 nm) photolysis of Cl_2–$SiHCl_3$ mixtures in the presence and absence of O_2 and other reactants were examined in attempts to establish the kinetics and mechanism for the Cl + $SiHCl_3$ reaction and to characterize the subsequent oxidation of the primary free radical $SiCl_3$. The possible occurrence of both H-atom abstraction and addition/displacement channels was considered first, i.e.

$$Cl + SiHCl_3 \rightarrow HCl + SiCl_3 \tag{1a}$$

$$\rightarrow H + SiCl_4 \tag{1b}$$

Reactions 1a and 1b are known to be exothermic by 12 and 16 kcal/mol, respectively.[7,8] For the Cl + SiH_4 reaction, the H-atom

---

(1) See, for example: Atkinson, R.; Lloyd, A. C. *J. Phys. Chem. Ref. Data* **1984**, *13*, 315.

(2) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1985**, *89*, 1752.

(3) Weaver, J.; Meagher, J.; Shortridge, R.; Heicklen, J. *J. Photochem.* **1975**, *4*, 341.

(4) Kan, C. S.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1980**, *84*, 3411.

(5) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1981**, *85*, 877.

(6) NASA Panel for Data Evaluation. "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling"; Jet Porpulsion Laboratory: Pasadena, CA, 1983; JPL Publication No. 83-62.

(7) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, *Suppl. No. 2*.

0022-3654/85/2089-3725$01.50/0