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LARGE MOLECULES IN CARBON VAPOR

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March 1959

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ABSTRACT

The molecular orbital theory is used in appropriate semi-empirical forms to predict the properties of carbon vapor. The results indicate that linear polyatomic molecules :C = C = C - - - C = C: are the important species. Experimental results from the literature for C_3 are combined with the calculated conjugation or resonance energies and with the heats of formation of allene and ethylene to predict heats of formation for all larger carbon molecules. It is found that the odd species have closed shell structures and lower energies than the even species but that the even species should show greater electron affinity. Both of these results are consistent with the mass spectrometric results of Honig and of Chupka and Inghram. Molecular spectroscopic data on C_3O_2 are used to estimate the free energy function increments for the species above C_3.

The calculated partial vapor pressures predict C_5 to be the most abundant species in the saturated vapor even at 2000°K with C_7 becoming comparably abundant in the 2500 to 3000°K range. At higher temperatures even larger molecules should become important. The results are shown to be generally consistent with all reliable vaporization data provided the evaporation coefficients decrease rapidly for increasing molecular size and vary for different crystal surfaces of graphite.

The calculated electronic energy levels for C_2 and C_3 agree satisfactorily with the observed spectra and trends are predicted for both even and odd larger species. It is proposed that liquid carbon consists of essentially infinite linear chains of this type. Both entropy and energy considerations lead to predicted heats of fusion of about 10 kcal/gm atom at 4000°K; the agreement between the two values indicates at least the absence of any serious inconsistency.

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Mass spectrometric studies[1-3] have clarified the previously confused situation with respect to the heat of sublimation of graphite to monatomic carbon and have established the presence of C_2, C_3 and probably C_5 in the vapor. The effusion measurements of Thorn and Winslow[4] are plausibly interpreted on the basis of C_1, C_2, and C_3 with heats of vaporization of approximately 170, 194, and 184 kcal/mole, respectively. There remains, however, the evidence of the effusion experiments of Doehaerd, Goldfinger and Waelbroeck[5] with very small hole-to-interior surface ratios which indicates some additional vapor species with higher equilibrium pressure but an evaporation coefficient about 10^{-3} in the temperature range 2500-2700°K. In addition, the measurements of Bégué[6] and Basset[7] indicate vapor

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(1) H. A. Chupka and M. G. Inghram, J. Chem. Phys. 22, 1472 (1954).

(2) R. E. Honig, J. Chem. Phys. 22, 126 (1954).

(3) H. A. Chupka and M. G. Inghram, J. Phys. Chem. 59, 100 (1955).

(4) R. J. Thorn and G. H. Winslow, J. Chem. Phys. 26, 186 (1957).

(5) T. Doehaerd, P. Goldfinger and F. Waelbroeck, Bull. Soc. Chim. Belg. 62, 498 (1953).

(6) J. Bégué, Thesis, Paris, 1945; (6b) discussion by P. Goldfinger and F. Waelbroeck, Bull. Soc. Chim. Belg. 62, 545 (1953).

(7) J. Basset, Chemie & industrie 45, 36, 7 (1941);
J. Basset, Brennstoff-Chem. 23, 127 (1942);
J. Basset, J. phys. radium 10, 217 (1939).

pressures reaching 1 atmosphere substantially below 4000°K which likewise require additional vapor species besides C_1, C_2, and C_3.

In seeking an explanation for these latter observations, we were led to a general consideration of the bi-coordinate state of carbon. A long chain of localized double bonds, alternately in the x and y planes, is quite unstable as compared to graphite. However, complete resonance or conjugation such that each bond is axially symmetric yields a large stabilization. Carbon dioxide provides the most familiar example of this type of binding. Carbon suboxide O=C=C=C=O provides a better example and use will be made of data on this compound below. The simplest form of molecular orbital theory is first applied to the linear C_n species and qualitative conclusions drawn. Then quantitative calculations are made and the results compared with the experimental data. Ring molecules are also considered and found to be unimportant under most conditions.

Simple Molecular Orbital Theory. First we consider the general pattern of orbital energies in order to determine which orbitals are occupied in the stable states of the various molecules. Orbital energies were calculated by the methods of Mulliken and his collaborators[8] in which the overlap integral is used as a measure of bond strength. Since we seek only a semi-quantitative estimate of orbital energies, no attempt was made to refine the empirical parameters. For sigma orbitals $\beta = -8.0\,\underline{S}$ and for pi orbitals $\beta = -10.5\,\underline{S}$, where $\underline{S}$ is the overlap integral and the units are e.v.; the promotion energy from 2s to 2p atomic orbitals was taken as 8.0 e.v. Overlap integrals are taken for Slater orbitals with $\underline{Z} = 3.25$. The resulting energy levels for C_2 and C_3 are shown in Figs. 1 and 2, respectively. In Fig. 4 is the band pattern for a very long linear carbon chain. The reduced bond distance $\rho = \underline{Z}\,\underline{R} / 2\,\underline{a}_o$ has a value near 4 for the low energy states we are considering.

The situation for C_2 has been admirably discussed by Mulliken[9] but it seems desirable to review it briefly for comparison with the larger molecules. There are 8 valence electrons which fill the lowest σ_g and σ_u levels and leave

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(8) R. S. Mulliken, J. Phys. Chem. 56, 295 (1953); R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

(9) R. S. Mulliken, Phys. Rev. 56, 778 (1939).

4 electrons to be placed in the π_u and the σ_g' orbitals. Since the π_u level is doubly degenerate with respect to orbital angular momentum as well as spin, it can accommodate 4 electrons. At the equilibrium C - C distance of approximately 1.3 A or $\rho = 4.0$, the calculated energies of the π_u and σ_g' levels are nearly the same and we expect several low lying electronic states as follows:

$$- - \pi_u\ (4)\ :\ {}^1\Sigma_g^+$$

$$- - \pi_u\ (3)\ \sigma_g'\ (1)\ :\ {}^3\Pi_u,\ {}^1\Pi_u$$

$$- - \pi_u\ (2)\ \sigma_g'\ (2)\ :\ {}^3\Sigma_g^-,\ {}^1\Delta_g,\ {}^1\Sigma_g^+$$

It is now quite well established that the ${}^3\Pi_u$ state is lowest with the ${}^3\Sigma_g^-$ state observed at 5656 cm^{-1} (0.70 ev, or 16.2 kcal/mole) by Ballik and Ramsay[10] and the ${}^1\Sigma_g^+$ state, based upon π_u (4), at 8 ± 4 kcal/mole (0.35 ev) as observed by Hicks.[11] The other states are at higher energies.

Since the triplet states allow somewhat better electron correlation in the complete wave function, the observed states are consistent with an orbital diagram like Fig. 1 in which the π_u level is a little lower than the σ_g' level at the observed distance. The separation at $\rho = 4.0$ in Fig. 1 is probably a bit too large, however. One may also note that the slope of the π_u level is positive and that of the σ_g' negative near $\rho = 4$. Consequently, one may predict, as Mulliken did, that the C - C distance will be least in the ${}^1\Sigma_g^+$ state, intermediate in the ${}^3\Pi_u$ state, and longest in the ${}^3\Sigma_g^-$ state.

With this confirmation of the method of calculation we turn now to the diagram for C_3, Fig. 2. The 12 valence electrons completely fill the orbitals as follows: σ_g (2), σ_u (2), σ_g' (2), π_u (4), σ_u' (2). Thus one predicts a ${}^1\Sigma_g^+$ ground state. Two configurations should yield excited states at energies

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(10) E. A. Ballik and D. A. Ramsay, J. Chem. Phys. 29, 1418 (1958).

(11) W. T. Hicks, Ph. D. Dissertation, University of California, 1957.

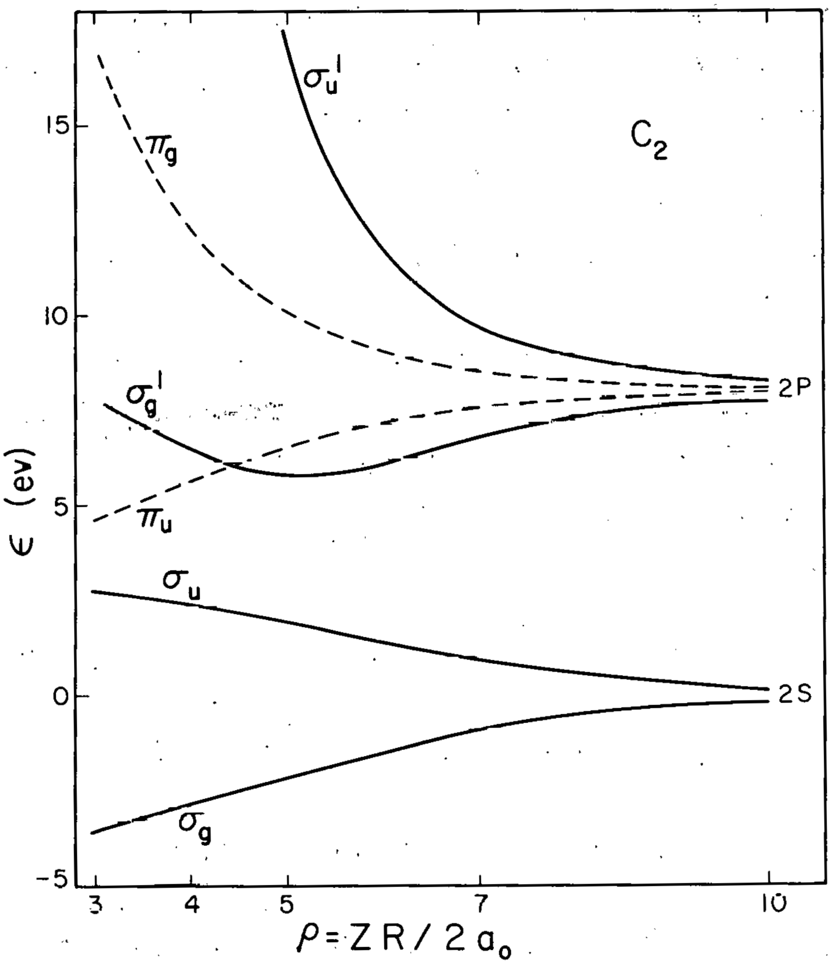

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Fig. 1. Electron orbital energy pattern for C_2.

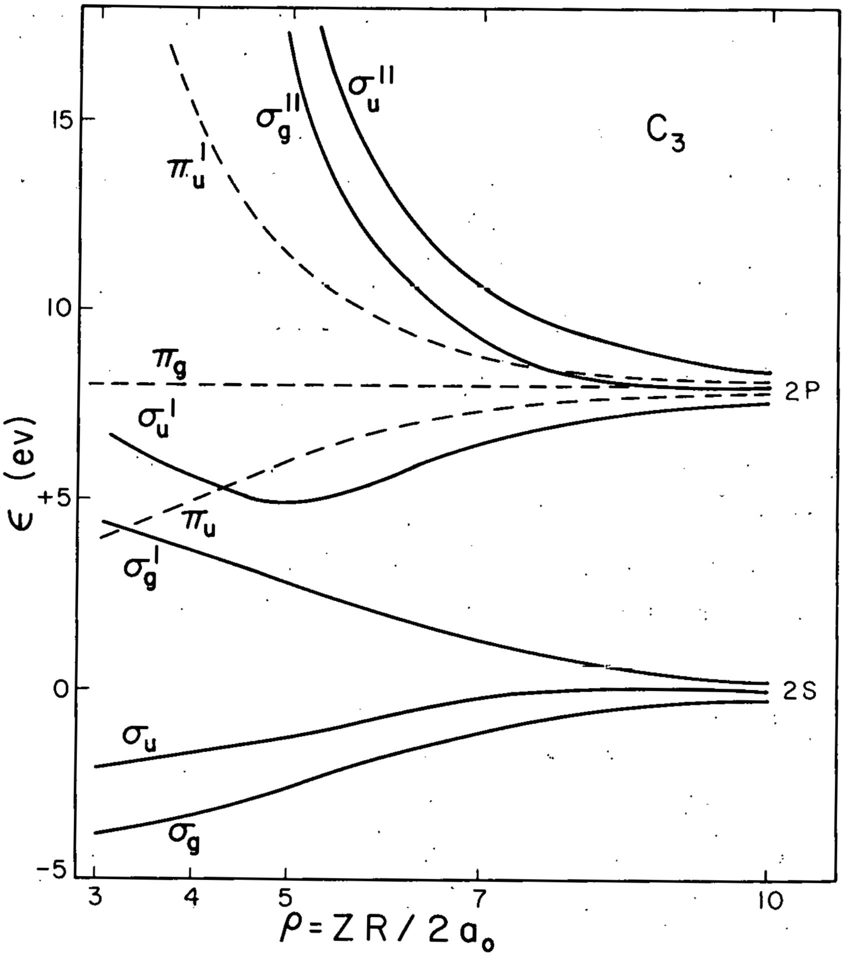

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Fig. 2. Electron orbital energy pattern for C_3.

in the vicinity of 3 ev as follows:

$$- - - \pi_u\,(4),\ \sigma_u{}'\,(1),\ \pi_g\,(1) :\ {}^3\Pi_u,\ {}^1\Pi_u$$

$$- - - \pi_u\,(3),\ \sigma_u{}'\,(2),\ \pi_g\,(1) :\ {}^3\Delta_u,\ {}^1\Delta_u,\ {}^1\Sigma_u{}^+,\ {}^3\Sigma_u{}^+,\ {}^1\Sigma_u{}^-,\ {}^3\Sigma_u{}^-$$

The energies of these various states for C_3 were obtained from the orbital energies of Fig. 2 and the electron repulsion terms which were estimated from corresponding terms of C_2 and O_2 but reduced for the greater distances in C_3. The energy level diagram in Fig. 3 shows also the two permitted transitions, ${}^1\Pi_u - {}^1\Sigma_g{}^+$ and ${}^1\Sigma_u{}^+ - {}^1\Sigma_g{}^+$. The observed absorption near 4050 A (3.06 ev) is presumably to be ascribed to the ${}^1\Pi_u \longleftarrow {}^1\Sigma_g{}^+$ transition.[12]

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(12) N. H. Kiess and H. P. Broida, Can. J. Phys. 34, 1971 (1956);
K. Clusius and A. E. Douglas, ibid, 32, 319 (1954);
A. E. Douglas, Astrophys. J. 114, 466 (1951);
G. Herzberg, Mém. soc. roy. sci. Liège 15, 291 (1955).

The lowest states based upon configurations with two electrons excited were estimated to lie above 4 ev, consequently the diagram in Fig. 3 may be regarded to be complete up to that level.

As the length of the molecule increases, the levels rapidly fall into the band pattern of the infinitely long chain, Fig. 4. Shockley[13] has shown that, in a case such as this, there are two terminal orbitals (hereafter written t orbitals) which split off, one each from the upper and lower σ bands, as ρ decreases below the point where the 2s and 2p band intersect. These t orbitals have most of their amplitude on the terminal atoms and decrease rapidly toward the middle of the chain. They are degenerate for an infinite chain. The $\sigma_g{}'$ and $\sigma_u{}'$ levels of C_3 are already beginning to show the behavior of t orbitals.

For a molecule C_n there are 4 n valence electrons. The lower σ band has n-1 orbitals and accommodates 2 n - 2 electrons and the t orbitals accommodate

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(13) W. Shockley, Phys. Rev. 56, 317 (1939).

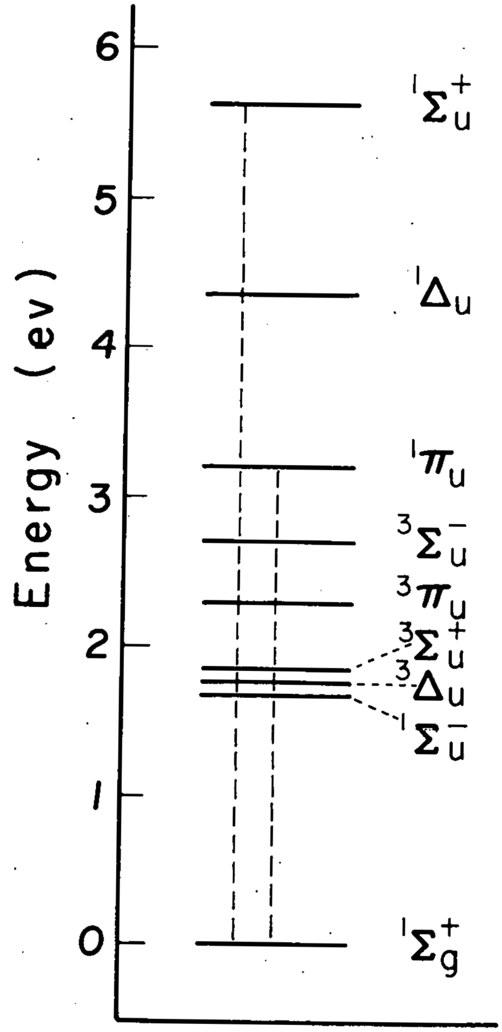

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Fig. 3. Estimated energies of the lower energy states of C_3. The diagram is incomplete above 4 ev. The dotted lines indicate allowed transitions.

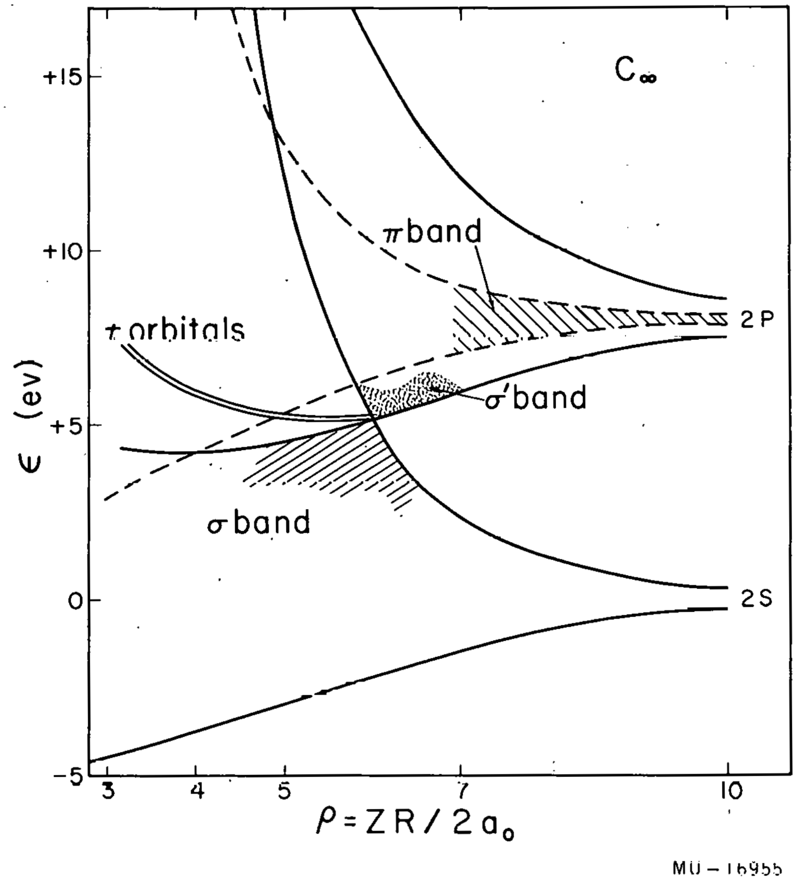

Fig. 4. Electron orbital energy bands for long linear C_n. The curves marked t-orbitals are for the pair of orbitals associated primarily with the terminal carbon atoms.

4 electrons. There remain 2 n - 2 electrons to be accommodated in the π band. At a distance near $\rho = 4$, the σ' band is, of course, empty in the ground state or low-lying excited states.

Since the orbitals of the π band accommodate 4 electrons each, molecules with n odd will just fill the lowest (n - 1)/2 of the π orbitals and will have $^1\Sigma_g^+$ ground states. Molecules with an even number of carbon atoms will completely fill the lowest ($\frac{1}{2}$ n - 1) of the π orbitals and place 2 electrons in the next higher π orbital. This will yield a $^3\Sigma_g^-$ ground state with $^1\Delta_g$ and $^1\Sigma_g^+$ states based on the same configuration at slightly higher energies.

Low-lying excited states (for n even or odd) will be obtained by exciting an electron from either the highest filled π orbital or a t orbital to the lowest empty or partially filled π orbital. The required energy for t electron excitation should be approximately 2 ev for n odd or large and even but may be less than 1 ev for C_4. The energy for π electron excitation will decrease from about 2 ev for C_5 or C_6 to very small values for long chains which will be one dimensional metals.

The discussion has implicitly assumed approximate uniformity of bond distance. Even n species might be considered in terms of an alternating triple bond single bond structure with single electrons at each end, but our estimates place this structure at substantially higher energy.

Let us restate the description of the long chain C_n molecules in more conventional chemical valence language. The bond structure is

$$:C = C = C = C = - - - - C = C:$$

where all intermediate atoms are contributing 2 electrons to the σ bonding system to form bonds with each adjacent atom and the terminal atoms use 3 electrons to form one σ bond and an unshared pair. The σ bonds comprise the σ band of Fig. 4 and the unshared pairs the two t orbitals. Thus there are 2 n - 2 electrons forming π bonds which are delocalized with respect to the x and y planes. Thus the bonding is analogous to $O = C = O$ or $O = C = C = C = O$ rather than to allene.

Quantitative Energy Calculations. It seems best to use some semi-empirical system of energy calculation which has proven successful for conjugated hydrocarbon molecules, since these are most analogous to the C_n molecules. The method of Mulliken, Rieke, and Brown[14] (MRB) was chosen together with the improved modification by Lofthus.[15] In the latter, both Slater and self-consistent field atomic orbital overlap integrals were used and are designated (L-S) and (L-F), respectively. These treatments apply only to the π electron system, and we use the methods and constants without change to obtain the conjugation energy of the π system.

First, however, we must obtain the energy of the hypothetical molecule with localized double bonds. This is done in two stages. The energy of interior atoms in a chain is taken from the energy difference allene-ethylene. The heats of formation of these compounds are accurately known[16] and those values, in turn, are corrected for the hyperconjugation present by the (MRB), (L-S), and (L-F) methods. The results are given in Appendix I and each is used self-consistently with the corresponding conjugation energy for the C_n molecule.

There is no satisfactory example of the terminal carbon atom of C_n in an ordinary substance of accurately known heat of formation. Carbon monoxide is the best available example but it seems unlikely that the large resonance energy of that molecule can be calculated accurately enough at present to make it a useful point of reference. Consequently, the energy of C_3 is taken as a reference point. It is assumed that the mass-spectrometer experiments of Chupka and Inghram[3] with an effusion cell source gave an equilibrium ratio of C and C_3 molecules. Their assumption of a 1 to 3 ratio of ionization cross sections is also retained. Any effect of the small difference in appearance potential between C and C_3 is ignored. The vapor pressure of C is computed

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(14) R. S. Mulliken, C. A. Rieke, W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).

(15) A. Lofthus, J. Am. Chem. Soc. 79, 24 (1957).

(16) F. D. Rossini, et al, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

from the free energy function discussed later and the value 169.58 kcal/mole for the heat of formation from graphite at 0°K.[17] Use of the free energy function of C_3 then yields a value of ΔH_o^o for the formation of gaseous C_3 from each vapor pressure measurement. The value of ΔH_o^o is practically constant over the temperature range of Chupka and Inghram's measurements. The average is $\Delta H_o^o = 186.5$ kcal/mole. The uncertainty from the scatter of results at different temperatures is 0.2 kcal/mole, but other possible errors raise the absolute uncertainty to possibly two or three kcal/mole.

The calculation of molecular orbital energies for C_n linear molecules is analogous to that of hydrocarbons with alternate single and double bond (including the end effect already discussed for the case of C_n polymers). The same may be stated for ring C_n polymers. Assuming the molecular axis is in the z direction, the two $2p_\pi$ orbitals point in the x and y directions (or the two π orbitals may be taken to have $\pm$ 1 angular momentum). Thus the double bonds are in the xz and yz planes.

The molecular orbital energies are solutions of a secular determinant of the form[15]

$$| \beta_{ij} + S_{ij} x_{ij} | = 0 \tag{1}$$

where S_{ij} is the overlap integral. The bond integral β_{ij} is defined in terms of the resonance integral

$$\gamma_{ij} = \int \varphi_i^* H \varphi_j \, d\tau \tag{2}$$

by the equation

$$\beta_{ij} = \gamma_{ij} - \tfrac{1}{2} S_{ij} (\alpha_{ii} + \alpha_{jj}) \tag{3}$$

also

$$x_{ij} = \tfrac{1}{2}(\alpha_{ii} + \alpha_{jj}) - \epsilon \tag{4}$$

where the atomic integrals α_{ii} depend in general upon the electronegativities for various atoms and ϵ is the energy of the molecular orbital. For the case of a C_n chain $\alpha_{ii} = \alpha_o$ because all the C atoms have the same electronegativity.

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(17) L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956).

If zero overlap integral is assumed (M.R.B.), then $\gamma_{ij} = \beta_{ij}$. The integral β_{ij} varies with internuclear distance, and its value is fixed for a standard bond length and then varied through a coefficient ρ_{ij}. Lofthus takes ρ_{ij} as the ratio of the overlap integral for the bond in consideration to the standard overlap integral.

Three sets of calculations for the molecular orbital energies were carried out. The first (M.R.B.) assumes zero overlap integral, the second (L-S) uses Slater's atomic orbitals for the overlap integrals, the third (L-F) uses self-consistent field atomic orbitals for the overlap integrals.

With zero overlap integral and considering only nearest neighbor interaction, the secular equation (1) is satisfied by the solutions of the form[19,20]

$$\epsilon_i = \beta_o K_i = \beta_o \left(2 \cos \frac{i\pi}{2n+1}\right) \quad (i = 1,2, --- , n). \qquad (5)$$

Because of the equivalent of the x and y directions for π electrons, each orbital is doubly degenerate and can accommodate four electrons.

If the overlap integral is evaluated, and if only nearest neighbors are considered to interact, then the solutions of Eq. (1) are of the form

$$\epsilon_i = \frac{K_i}{1 + SK_i} \beta_o \quad . \qquad (6)$$

The values for overlap integral at 1.28 A are 0.299 for Slater orbitals and 0.395 for self-consistent field atomic orbitals.

For each of the three sets of calculations, the conjugation energy is obtained as the difference between the delocalized total energy for the bond distance 1.28 A (observed for C_3) and the localized total energy which is (n - 1) times the standard double bond energy at the standard bond distance. The ρ values for 1.28 A are 1.155, 1. 125, and 1.090 in the (M.R.B.), (L-S), and (L-F) systems, respectively, and the corresponding standard β_o values (and standard distances) are 44.5 kcal/mole (for 1.33 A), 81 kcal/mole

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(19) E. Hückel, Z. Physik 70, 204 (1931).
E. Hückel, Z. Physik 76, 628 (1932).

(20) J. E. Lennard-Jones and J. Turkevich, Roy. Soc. London Proc. A 158, 280 (1937).
C. A. Coulsen, ibid, A 169, 413 (1939).

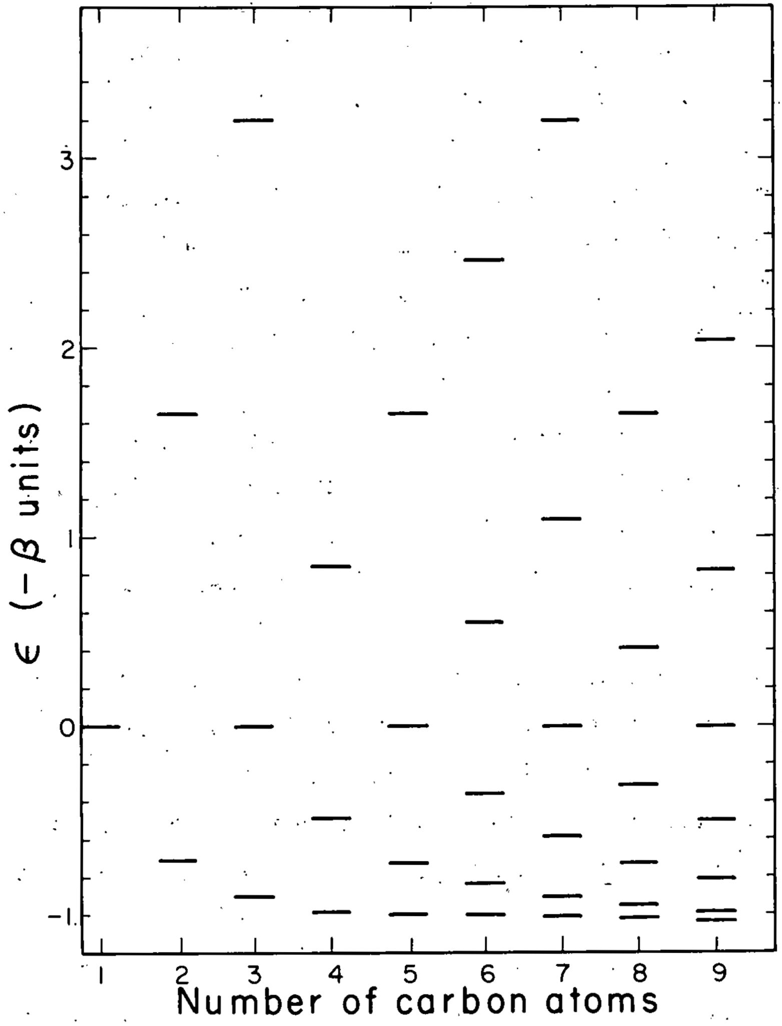

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Fig. 5. Calculated molecular orbital energies for linear molecules C .

(for 1.353 A) and 102 kcal/mole (for 1.353 A). Fig. 5 shows the calculated molecular orbital energies in the (L-F) system for C_1 to C_9. The highest energy levels for C_4 - C_9 fall above the top of the figure.

As discussed in the Appendix the contribution to ΔH_o^o of formation per interior carbon atom in a molecule with localized π bonds is 48.323, 43.112, and 43.408 kcal/mole for the M.R.B. (L-S), and (L-F) methods respectively. Assuming the value of 186.5 kcal/mole as ΔH_o^o of formation for C_3, the heat of formation for C_n is 186.5 plus ($\underline{n}$ - 3) times the heat of formation for an interior carbon atom less the difference of conjugation energy between C_n and C_3.

For chains with an even number of carbon atoms the calculation yields a value appropriate for the $^1\Delta$ state. The correction to the $^3\Sigma$ ground state is estimated to be -23/n kcal/mole (see discussion on C_2 energy levels). This value decreases very rapidly and reaches a value less than .7% of the heat of formation at C_{10}.

While there is a gradually increasing divergence between the three series of calculated values of ΔH_o as shown in Table I, nevertheless the same general pattern is given in each case with the odd species more stable. The (L-F) series has the best theoretical basis and it seems likely that these values are correct within 15 kcal/mole through C_7 but may err by increasing amounts for larger n.

In addition to the results for molecules through C_{13} shown in Table I, ΔH_o^o of formation values were calculated by the L-F method for C_{14} (302.9), C_{15} (294.1), C_{16} (324.8), C_{17} (318.1 kcal/mole), and for the infinite chain, 12.7 kcal/gm atom of carbon.

Table I

Calculated values for ΔH_o^o of formation* (kcal/mole)

C_n	M. R. B.	(L-S)	(L-F)
C_4	212.6	218.3	224.5
C_5	190.2	187.9	193.3
C_6	214.3	220.4	232.9
C_7	198.6	196.9	208.8
C_8	220.0	227.2	246.3
C_9	208.7	209.1	228.0
C_{10}	228.0	236.9	263.3
C_{11}	219.8	222.8	249.2
C_{12}	237.6	248.8	282.4
C_{13}	230.9	237.2	271.7

*For C(gas), C_2 and C_3, the observed value of ΔH_o^o of formation are 169.58, 200, and 186.5 kcal/mole, respectively.

Free Energy, Entropy, and Enthalpy Functions. In order to calculate the equilibrium vapor pressures of the various C_n species it is necessary to obtain the function $-(F_T^o - H_0^o)/T$ for each. The values for atomic carbon and graphite are well established.[16]

The functions for C_2 were calculated by Gordon.[21] To these values a small correction was added for the ${}^1\Sigma_g^+$, ${}^3\Sigma_g^-$, and ${}^1\Pi_u$ states where energies have been recently determined. The values of Kelley[22] and of Stull and Sinke[23] err by a factor of two in the multiplicity of the ${}^3\Pi_u$ state.

Glockler[24] calculated the free energy function for C_3 and Stull and Sinke adopt his values. However, the analysis above indicates a multiplicity of one rather than five for the ground state of C_3. Also, a comparison of the analogous potential constants with those of C_3O_2, ketene, and allene suggested somewhat higher vibration frequencies which were adopted: $\nu_1 = 1300$, $\nu_2 = 550$ (degenerate), and $\nu_3 = 2200$ cm^{-1}.

The largest percentage change is in ν_2 where Glockler used 353 cm^{-1}. This is the lowest bending frequency of allene, and correction for the absence of the mass of the hydrogen atoms would substantially raise this frequency. Evidence for a value near 550 cm^{-1} comes also from the emission spectrum of C_3, observed by Kiess and Broida.[12] This shows a 523 cm^{-1} frequency difference between band heads 21 times, and these authors suggested interpretation as the bending frequency of C_3.

The rotational constant of C_3 is known accurately from the spectrum to be 0.4280 ± .0005 cm^{-1} which corresponds to a C - C distance of 1.281 A.

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(21) A. R. Gordon, J. Chem. Phys. 5, 350 (1937).

(22) K. K. Kelley, U. S. Bureau of Mines Bulletin 477 (1950).

(23) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956.

(24) G. Glockler, J. Chem. Phys. 22, 159 (1954).

The best basis now available for estimating the increment to a thermodynamic function on increase from C_n to C_{n+1} is one-half the difference between C_3O_2 and CO_2. The functions of the latter are well known;[16] those of C_3O_2 were calculated from the data of Long, Murfin, and Williams[25] and of Mackle and Sutton.[26] Unpublished infrared measurements of Williams in this laboratory give an improved value of 215 cm^{-1} for the lowest bending frequency.

The ground electronic state of C_4 and the larger molecules with n even is predicted to be a $^3\Sigma_g^-$ state whose multiplicity is 3. Other states for even molecules lie within the range of thermal energy but it would be an unjustified elaboration of our calculations to consider them in detail. It is estimated the contribution to the partition function from these excited states equals that from the ground electronic state, i.e., that the effective multiplicity is 6. Consequently, $\underline{R} \ln 6 = 3.56$ cal/deg mole must be added to the $-(F^o - H_o^o)/T$ and S^o values for all even species. If the $^3\Pi_u$ state of C_4 lies relatively close to the ground state, the effective multiplicity in that case might approach 9.

The resulting thermodynamic functions are presented in Tables II, III, and IV. The error in S or $-(F_T^o - H_o^o)/T$ for C and C_2 should be small and for C_3 not over 0.5 cal/deg mole. The first row in each case is for solid graphite[16] which is included for convenience in calculations. The first set of values for the increment per carbon atom above C_3 is based upon the C_3O_2 spectrum as described above. A modified set of values for this increment in $-(F^o - H_o^o)/T$ and S^o was obtained by adjustment to fit the observed triple point pressure of graphite, approximately 100 atm at 4000°K.[7] These modified values correspond to an increase in two of the three bending frequencies of C_3O_2 by about 30%. While this shift seems rather large, the possible errors in the use of C_3O_2 properties to predict the increment per additional carbon atom in a long chain are certainly of this magnitude.

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(25) D. A. Long, F. S. Murfin, and R. L. Williams, Proc. Roy. Soc. A223, 251 (1954).

(26) H. Mackle and L. E. Sutton, Trans. Faraday Soc. 47, 937 (1951).
R. L. Livingston and C.N.R. Rao, J. Am. Chem. Soc. 81, 285 (1959).

Table II

The free energy function* $-(F^o - H_o^o)/T$ in cal/deg mole

Substance		T^oK 2000	2500	3000	3500	4000
Graphite		5.37	6.39	7.28	8.07	8.78
C_1		42.215	43.334	44.251	45.029	45.707
C_2		56.39	58.27	59.82	61.22	63.35
C_3		61.82	64.59	66.93	68.95	70.73
Increment per C atom	(a)	9.57	10.60	11.49	12.24	12.91
	(b)	8.32	9.35	10.24	10.99	11.66

(a) Increment per carbon atom based upon C_3O_2.

(b) Increment per carbon atom adjusted to triple point pressure.

*3.56 cal/deg mole is to be added to the values for even n species (except C_2), see text.

Table III

The heat content function $(H^{o} - H_{o}^{o})/T$ in cal/deg mole

Substance	T°K				
	2000	2500	3000	3500	4000
Graphite	4.39	4.74	5.01	5.22	5.40
C_1	5.014	5.019	5.036	5.062	5.092
C_2	8.14	8.20	8.33	8.35	8.41
C_3	12.21	12.66	12.95	12.23	13.41
Increment per C atom	4.55	4.77	4.90	5.01	5.08

Table IV

The entropy* in cal/deg mole

Substance		T°K 2000	2500	3000	3500	4000
Graphite		9.76	11.13	12.29	13.29	14.18
C_1		47.223	48.353	49.287	50.090	50.798
C_2		64.532	66.470	68.147	69.569	70.764
C_3		74.03	77.25	79.89	82.18	84.14
Increment per C atom	(a)	14.12	15.37	16.39	17.25	17.99
	(b)	12.87	14.12	15.14	16.00	16.74

(a) Increment per carbon atom based upon C_3O_2.

(b) Increment per carbon atom adjusted to triple point pressure.

*3.56 cal/deg mole is to be added to the values for even n species (except C_2), see text.

Calculated Vapor Pressures and Vapor Enthalpies. By combination of the ΔH_o of formation values with the $-(F_T^o - H_o^o)/T$ values of Table II, the vapor pressure at equilibrium of each species C_n may be calculated. The results for each of the three conjugation energy methods are given in Table V through C_7.

When the vapor pressure calculations were first completed, it was evident that the predicted pressures of long chain molecules were extremely large in the 3500 - 4000°K range. The L-F energies gave the lowest pressures but even these were too high to be consistent with the observed sublimation pressure[6] of 1 atm near 3700°K, and the triple point pressure[7] of about 100 atm at 4000°K. While these data are subject to considerable uncertainty, the most likely errors[27] would raise the temperatures assigned and make the inconsistency greater. Consequently, it seemed likely that our $-(F^o - H_o^o)/T$ increment per C atom, estimated from the C_3O_2 spectrum, was too large and that this error, multiplied by (n - 3), was the primary cause of the disagreement. As stated above, a revised value of the increment per C atom was selected to yield approximately 100 atm total pressure at 4000°K with the L-F energies. It is some compensation, at least, that the L-F series, which is the best founded theoretically, also yields the most reasonable pressures.

Figure 6 shows the calculated values of log P for the various species C_n based upon the (L-F) energies and the revised free energy function values. The alternation of the values for the pressure between even and odd carbon species is quite evident. This result is due to the alternation in the pattern of filling of molecular orbitals for the odd and even species as discussed above. The mass spectrographic data[2] show this alternation through C_5, the highest species observed.

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(27) See L. Brewer, J. Chem. Phys. 16, 1165 (1948).

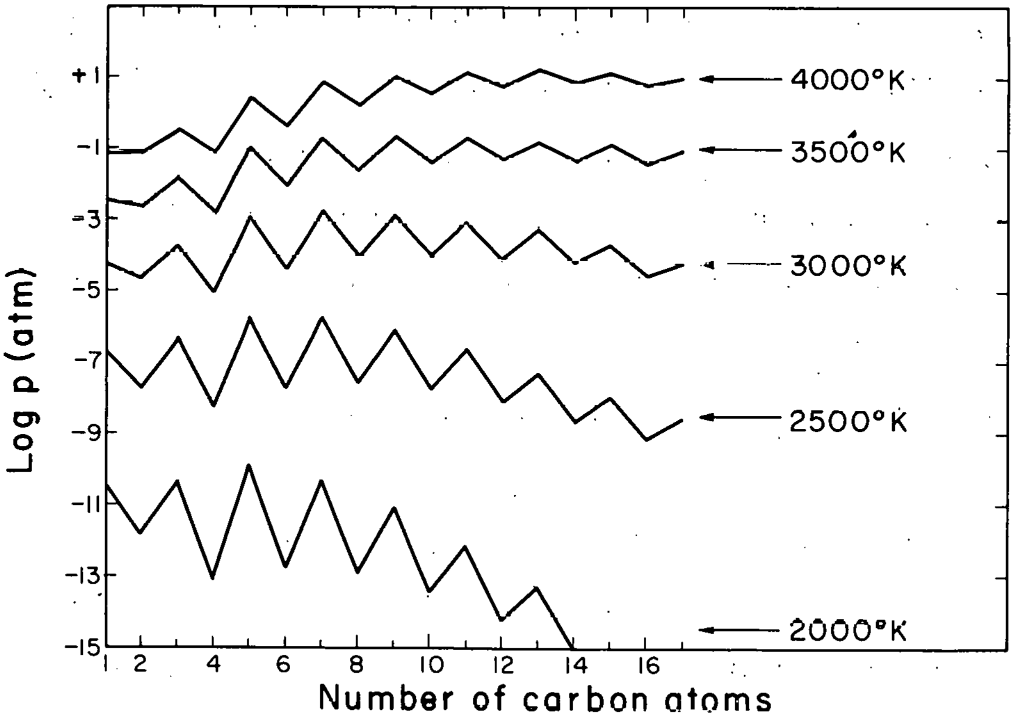

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Fig. 6. Calculated partial pressures of the various vapor species C_n in equilibrium with graphite at several temperatures.

Table V

Calculated values of log P (atm) of various carbon vapor species in equilibrium with graphite

Substance		T°K 2000	 2500	 3000	 3500	 4000
C_1		-10.478	-6.75	-4.274	-2.512	-1.195
C_2		-11.87	-7.76	-4.67	-2.64	-1.14
C_3		-10.40	-6.39	-3.74	-1.87	-0.49
C_4	(a)	-11.81	-7.17	-4.12	-1.97	-0.37
	(b)	-12.18	-7.47	-3.37	-2.17	-0.55
	(c)	-13.03	-8.20	-4.97	-2.70	-1.06
	(d)	-13.12	-8.28	-5.08	-2.83	-1.12
C_5	(a)	- 9.19	-5.05	-2.32	-0.41	1.00
	(b)	- 8.73	-4.68	-2.01	-0.14	1.23
	(c)	- 9.32	-5.14	-2.39	-0.47	0.94
	(d)	- 9.84	-5.67	-2.93	-1.01	-0.42
C_6	(a)	-10.11	-5.44	-2.37	-0.21	1.37
	(b)	-10.54	-5.79	-2.66	-0.46	1.16
	(c)	-11.89	-6.87	-3.56	-1.23	1.08
	(d)	-12.74	-7.71	-4.39	-2.07	-0.34
C_7	(a)	- 8.26	-3.94	-1.09	0.89	2.35
	(b)	- 7.87	-3.62	-0.89	1.24	2.55
	(c)	- 9.16	-4.66	-1.68	0.38	1.90
	(d)	-10.89	-5.74	-2.77	-0.70	0.83

(a), (b), (c) Values for M.R.B., L-S, and L-F methods, respectively, with free energy function increment based upon C_3O_2.

(d) Values for L-F method with free energy function increment adjusted to triple point pressure.

In addition to the calculations of the partial vapor pressures, the total vapor pressure, the mean number of carbon atoms per molecule $\bar{n}$, and the enthalpy per gm atom and per mole were calculated on the basis of the L-F energies and the adjusted free energy function increments. These values, which are for the saturated vapor in equilibrium with solid graphite, are given in Table VI. More significant figures are retained for $\bar{n}$ in Table VI than the absolute accuracy would justify in order to avoid errors in the use of the molal enthalpy values. The negative apparent heat capacity per gram atom of the saturated vapor is an interesting result of the rapid increase of molecular size with increase in temperature.

It is evident from Table V and Fig. 6 that at 2000°K and above, our calculations predict C_5 and C_7 to be very important species in equilibrium carbon vapor. At high temperatures even larger molecules become important, although the uncertainties of calculation make this more a qualitative than a quantitative prediction. For comparison with the effusion experiments of Doehaerd, Goldfinger, and Waelbroeck[5] it is convenient to restate our results in terms of an apparent heat of sublimation of monoatomic carbon, the only specie considered by the above authors. If we denote this quantity by ΔH_{ap}, then for effusion experiments

$$\Delta H_{ap} = 169.5 - R\,T \ln \frac{\Sigma_n\, n^{1/2}\, P_n}{P_1} \tag{7}$$

where the P_n are the partial pressures of the species C_n. The approximate temperature of the experiments is 2600°K. Using the partial pressures given by (L-F) method adjusted to the triplet point pressure, one obtains from Eq. (7) $\Delta H_{ap} = 145.6$ as compared with a value of 143.2 given by Doehaerd, Goldfinger, and Waelbroeck.[5] Any of the other sets of calculated pressures yields a lower ΔH_{ap}. This agreement is all that could be expected and clearly

Table VI

Properties of carbon vapor in equilibrium with graphite

(Ref. point for H, graphite at 0°K)

T, °K	log P (total) atm	$\bar{n}$ = mean no. atoms	H_T, kcal per gm atom	H_T, kcal per mole
2000	-9.54	4.777	53.3	255
2500	-5.25	6.231	44.2	276
3000	-2.21	8.137	41.3	336
3500	+0.14	10.87	40.3	438
4000	2.01	13.45	39.2	527

removes any disagreement between the effusion data and theoretical expectations based on the 169.58 kcal/mole heat of sublimation of monatomic carbon.

Taken at face value this agreement of apparent ΔH values also indicates that the evaporation coefficients of all species through C_7 at least are large enough to have yielded near equilibrium pressures with the aperture to surface ratio of 1 to 23,400. However, Doehaerd, et al., assumed the value of 0.2 for the sticking coefficient of carbon vapor on a relatively hot receiver. This value was obtained by Simpson, Thorn, and Winslow[28] under similar but not identical conditions. While Doehaerd, et al., realized that there was uncertainty in transferring the sticking coefficient value to their experiments, that uncertainty seemed moderate if carbon vapor was purely monatomic. We now know that the vapor is a complex mixture of several gaseous species each of which has its own sticking coefficient. Consequently the Doehaerd, et al., value of ΔH_{ap} is subject to as much as 7 kcal/mole uncertainty, and the possibility remains that their conditions yielded less than equilibrium amounts of C_5 and larger species.

The effusion cells used by Thorn and Winslow[4] had aperture to surface ratios of about 1 to 2000 (about ten times that of Doehaerd, et al.) but cooled receivers eliminated the sticking coefficient uncertainty. Their ΔH_{ap} = 161.0 kcal/mole at about 2450°K corresponds quite closely to an equilibrium vapor through C_3 with higher species absent. Thorn and Winslow interpreted their data on this basis and calculated properties of C_3 very similar to those we selected. From this result one may conclude that the evaporation coefficients

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(28) O. C. Simpson, R. J. Thorn, and G. Winslow, AECD-2680 (1949).

for C_5 and larger species are distinctly less than 5×10^{-4} under the conditions of the Thorn and Winslow experiments.

Also there is the older work of Brewer, Gilles, and Jenkins[29] and of Brewer and Mastick[30] which Thorn and Winslow[4] described in 1957 as "probably the most reliable effusion experiment prior to presently reported one." Brewer, et al, used a cooled receiver and found a sticking coefficient of 0.45. The aperture to evaporating surface ratio is not available because they partially filled their cell with graphite powder of unknown surface area. The values of ΔH_{ap} range from 150.9 to 166.8 kcal/mole at 2600°K but the low values always were obtained on the first run with a fresh sample of graphite powder. Later runs with the same sample gave higher values eventually reaching the range 165 ± 2 kcal/mole which one interprets as indicating an equilibrium amount of C and C_2 with some C_3.

Brewer, Gilles, and Jenkins interpreted the drift in their ΔH_{ap} values as due to "volatilization of tars remaining in the material from the binder used in the graphitization process." Since the evaporation coefficients of the polyatomic carbon molecules probably vary greatly for different surfaces of graphite, it now seems more likely that in the early runs the evaporation rates of C_3 and C_5 were substantial but that these rates fell off as the reactive (high evaporation coefficient) surfaces were depleted. This explanation seems reasonable in terms of the structure of graphite and the possible mechanisms for breaking off a C_3 or C_5 molecule.

Finally, there are the measurements of Begue[6a] which are interpreted to indicate a total vapor pressure of carbon one atmosphere at about 3750°K. The values in Table VI show a total pressure of one atmosphere at a little below 3500°K. These results are not necessarily inconsistent because the evaporation coefficients of the very large carbon molecules may still be small at these temperatures. Since the observed temperatures are for conditions of

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(29) L. Brewer, P. W. Gilles, and F. A. Jenkins, J. Chem. Phys. 16, 797 (1948).

(30) L. Brewer and D. F. Mastick, University of California Radiation Laboratory report, UCRL-572 (1949); D. F. Mastick, Ph.D. thesis, University of California (1950); see also Ref. (6b).

rather rapid evaporation, they do not necessarily indicate the equilibrium vapor pressure curve. The same objection can be raised with respect to the sublimation point measurements of Basset,[7] but the error should decrease with rise in temperature and pressure.

Rings. It is possible to use many of these same methods to estimate the abundance of ring molecules in carbon vapor. Although the $= C = C = C = C =$ linkage tends to be linear it is somewhat flexible and a long linear molecule C_n may be bent into a ring whereupon the terminal unshared electron pairs will form another double bond. Thus all atoms have the basic valence state of interior atoms in the linear chain, and the conjugation energy of the π system is readily calculated for the ring by the same methods as for the chain. If $\underline{n} = 4\underline{k} + 2$ with $\underline{k}$ an integer, then a $^1\Sigma_g$ ground state results. The bending force constants for the central portion of the $O = C = C = C = O$ molecule may be used to estimate the strain energy of the C_n ring to be approximately $(1800/\underline{n})$ kcal/mole.

The entropy or free energy function for a ring is substantially smaller than that for a chain. By comparison with values for hydrocarbons we estimate this difference to be at least 20 and 25 cal/mole degree for C_{10} and C_{14} respectively. In the M.R.B. method the ring molecular orbital energies[20] are ± 2, ± 1.618 $\pm .618$ for C_{10} and ± 2, ± 1.802, ± 1.247 and $\pm .445$ for C_{14} in units of β. The M.O. of energy ± 2 accommodates two electrons; the others are doubly degenerate with respect to orbital angular momentum and accommodate four electrons. The resulting ΔH_0^o of formation values are 264 and 297 kcal/mole for C_{10} using (L-S) and (L-F) methods, respectively, and 271 and 322 for C_{14} ring with the corresponding methods.

In the range 2000-4000°K the calculated pressures of C_{10} and C_{14} rings are smaller than the pressures of the corresponding chains by factors ranging from 10^{-6} to 10^{-8}. Since the even-numbered linear species are already less abundant than the adjacent odd species, it is evident that ring molecules play no significant role in this region. Possibly rings would become important for very large $\underline{n}$ values but only under conditions where these exceedingly long chains were also abundant.

Negative Ions. Honig[2] noted the presence of substantial quantities of negative ions C_n^- in carbon vapor and found the even species to be the more abundant. This result follows clearly from the simple molecular orbital theory. The even neutral species C_n have a half-filled bonding π orbital which can accommodate another electron whereas in the odd species the extra electron must go into the empty non-bonding orbital.

The electron affinity calculations of Honig can be revised and extended by the use of the improved energy of C_3, the calculated energy of C_4, and the electronic multiplicities which we feel to be quite certain. The negative ions have $^2\Pi_u$ ground states, except C^- which is ^4S and C_2^- where the $^2\Sigma_u$ state may be slightly below $^2\Pi_u$. Honig[2] calculated electron affinities, where possible, by two methods; (a) the <u>difference</u> in the heats of formation derived from the temperature derivative of the abundances and (b) the <u>ratio</u> of the absolute intensities interpreted on the basis of assumed cross sections, etc., and equal electronic multiplicities for neutral and ion in each case. Introduction of our data yields the results of Table VII. The uncertainty in these values is about 1 ev in most cases.

Table VII

Electron affinity of carbon molecules

(electron volts)

Species	Difference value	Ratio value
C	-	1.4
C_2	4.0	3.2
C_3	2.4	1.7
C_4	3.6	-

With increase in length of the carbon molecule the oscillation of electron affinity between even and odd species will diminish because the available orbitals differ less in energy. This too is consistent with Honig's results. The limiting electron affinity for a very long chain should approach that of graphite, 4.4 ev.

Liquid Carbon. Since the calculated properties of carbon vapor (after the adjustment in the free energy function) seem to be in reasonable accord with all observed properties, it is interesting to speculate about the nature of liquid carbon. It is difficult to picture a liquid based on the graphite structure, but the long linear polymer molecules certainly could form a liquid somewhat analogous to long n-paraffins or sulfur in the range above $160^{\circ}C$ where the equilibrium shifts from S_8 ring molecules to long chains. The carbon chains do not have the zig-zag structure of sulfur or a n-paraffin, with the possibility of rotation about single bonds. Consequently, carbon chains would be less flexible in terms of a given thermal energy, but at $4000^{\circ}K$ carbon chains would be sufficiently flexible to form a disordered liquid-like phase.

Let us assume for liquid carbon the entropy per added carbon atom of long chains in the gas, which from Table IV is 16.82 cal/deg gm atom at $4000^{\circ}K$. The heat of formation of liquid at $4000^{\circ}K$ is taken as the heat of formation per added carbon atom (given above for $0^{\circ}K$ and corrected to $4000^{\circ}K$) of 11.4 kcal/gm atom less an estimated value of 1.0 kcal/gm atom for the Van der Waals attractive forces between chains in the liquid state. The latter figure was estimated from a comparison of the heats of vaporization of C_3O_2 and CO_2. The corresponding quantity for long n-paraffins[16] is also about 1.0 kcal per mole of CH_2 units. The calculations of Coulson and Davies[31] indicate a larger value, possibly 3 to 4 kcal/gm atom, at an interchain distance of 3.4 A corresponding to the interplanar separation in graphite, but we estimate that the inclusion of overlap integrals neglected by Coulson and Davies would reduce this value to the range 1 to 2 kcal/gm atom.

Now we have two estimates of the heat of fusion. From the energy calculations, $\Delta H_f = 10.4$ kcal/gm atom; but from the entropy calculations, $\Delta H_f = T\,\Delta S_f = 4000\,(16.82 - 14.18)/1000 = 10.5$ kcal/gm atom. This agreement, which must be regarded as fortuitously good, nevertheless certainly supports the general model of long linear chains (and very large rings) for liquid carbon.

It is also interesting to calculate the heat of sublimation at $4000^{\circ}K$, which is 17.6 kcal/gm atom, and then by deducting the heat of fusion one obtains for the heat of vaporization of the liquid 7 kcal/gm atom. If these values are at all close to the true properties, the vapor pressure curve will show a very large decrease in slope at the melting point because the heat of fusion is larger than the heat of vaporization of the liquid.

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(29) C. A. Coulson and P. L. Davies, Trans. Faraday Soc. 48, 777 (1952).

Liquid carbon comprising long linear polymer molecules should be relatively viscous as is sulfur when it is in the polymeric state. Also, although the linear polymeric chains may be expected to be one dimensional metals, the macroscopic electrical conductance would be much less that of graphite with its two dimensional metallic character.

Acknowledgments. We are greatly indebted to Professor Leo Brewer for many discussions. Dr. W. Weltner Jr. has given us the benefit of his study of this problem and told us of recent work at the National Carbon Research Laboratories. This work was performed under the auspices of the U. S. Atomic Energy Commission.

APPENDIX

The conjugation energy (C.E.) for the interior atoms in the C_n chain is obtained from the difference in C.E. for allene and ethylene with a correction for compressional energy corresponding to contraction from the standard double bond to the 1.28 A bond assumed for the chain.

The C.E. is calculated following the M.R.B. method and the Lofthus modification of that method. M.R.B.[14] assume zero overlap integral, a reference double bond of 1.33 A (ethylene double bond) and a standard resonance integral β_o = -44.5 kcal/mole. Lofthus[15] uses overlap integrals calculated with Slater or S.C.F. atomic orbitals. The reference double bond distance is 1.353 A. The β_o values are -81 and -102 kcal/mole for Slater orbitals or S.C.F. orbitals, respectively.

An additional correction of .5 β_o is introduced by Lofthus to account for the different electronegativity of the terminal hydrogen group as compared to the carbon atom. The secular equation (1) for allene and ethylene is solved for localized and delocalized bonds. The values for the β_o coefficients and for conjugation energy are given in Table VIII.

Table VIII

Orbital and conjugation energies of allene and ethylene

Method		Localized M.O. Coefficients		Delocalized M.O. Coefficients		Conjugation Energy
M.R.B.	Ethylene	4.000	--	4.531	3.531	0.124
	Allene	4.000	1.058	4.146	1.023	0.444
(L-S)	Ethylene	1.275	--	1.508	1.048	0.012
	Allene	1.277	0.845	1.432	0.720	0.121
(L-F)	Ethylene	0.945	--	1.177	0.718	0.008
	Allene	0.946	0.770	1.140	0.601	0.098

Compressional energies are obtained from a Morse potential assuming a dissociation energy D = 141.5 kcal/mole and a bond force constant of 8.2×10^5 dyne cm^{-1}.

The contribution to ΔH_o° of formation of the hypothetical C_n with localized bonds per interior carbon atom is then the difference in ΔH_o° of formation[16] between allene and ethylene (33.178 kcal/mole) corrected for the difference in their conjugation energies and compressional energies. If the compression energy to the 1.28 A band distance of C_3 (and presumably of longer C_n molecules) is added, the final values are 48.323, 43.112, and 43.408 kcal/mole for the M.R.B., (L-S), and (L-F) methods. These values are used in the calculations leading to Table I.