[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND COLLEGE OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Large Molecules in Carbon Vapor

BY KENNETH S. PITZER AND ENRICO CLEMENTI

RECEIVED APRIL 20, 1959

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 $:C{=}C{=}C{\cdots}C{=}C:$ 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./g. atom at 4000°K.; the agreement between the two values indicates at least the absence of any serious inconsistency.

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 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-coördinate 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 $\beta = -8.0S$ and for pi orbitals $\beta = -10.5S$, where 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 $Z = 3.25$. 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 $\rho = ZR/2a_0$ has a value near 4 for the low energy states we are considering.

The situation for C_2 has been discussed admirably 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 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 Å. 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

$$\cdots \pi_u\,(4){:}\ {}^1\Sigma_g{}^+$$
$$\cdots \pi_u\,(3)\ \sigma_g'\,(1){:}\ {}^3\Pi_u,\ {}^1\Pi_u$$
$$\cdots \pi_u\,(2)\ \sigma_g'\,(2){:}\ {}^3\Sigma_g{}^-,\ {}^1\Delta_g,\ {}^1\Sigma_g{}^+$$

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 e.v., or 16.2 kcal./mole) by Ballik and Ramsay[10] and the ${}^1\Sigma_g{}^+$ state, based

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

(2) R. E. Honig, *ibid.*, **22**, 126 (1954).

(3) W. 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) (a) J. Bégué, Thesis, Paris, 1945; (b) discussion by P. Goldfinger and F. Waelbroeck, *Bull. soc. chim. Belg.*, **62**, 545 (1953).

(7) J. Basset, *Chemie and industrie*, **45**, No. 3f, 7 (1941); *Brennstoff-Chem.*, **23**, 127 (1942); *J. phys. radium*, **10**, 217 (1939).

(8) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952); 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).

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

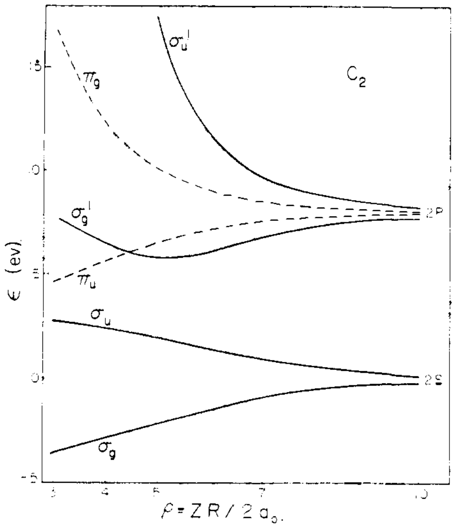

Fig. 1.—Electron orbital energy pattern for C_2.

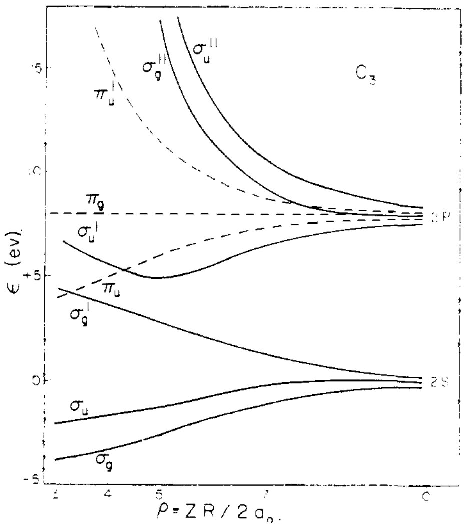

Fig. 2.—Electron orbital energy pattern for C_3.

upon π_u (4), at 8 ± 4 kcal./mole (0.35 e.v.) 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 in the vicinity of 3 e.v. as

--- π_u (4), σ_u' (1), π_g (1): $^3\Pi_u$, $^1\Pi_u$
--- π_u (3), σ_u' (2), π_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 Å. (3.06 e.v.) is presumably to be ascribed to the $^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition.[12]

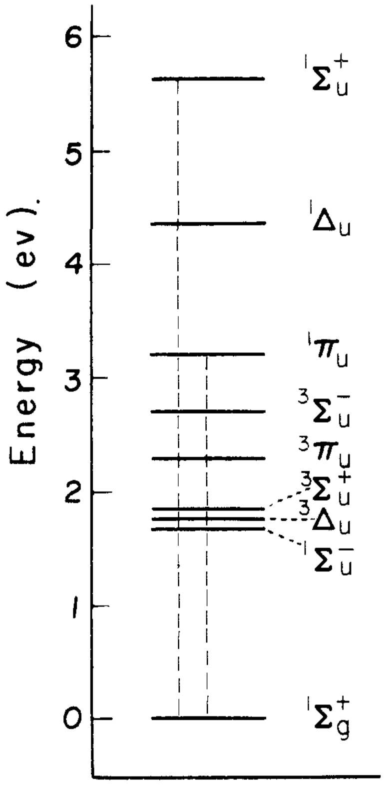

Fig. 3.—Estimated energies of the lower energy states of C_3. The diagram is incomplete about 4 e.v. The dotted lines indicate allowed transitions.

The lowest states based upon configurations with two electrons excited were estimated to lie above 4 e.v., 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 bands intersect. These t orbitals have most of their amplitude on the terminal atoms and decrease rapidly toward the middle of the chain. They are

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[11] W. T. Hicks, Ph.D. Dissertation, University of California, 1957.

[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).

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

degenerate for an infinite chain. The σ_g' and σ_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 $2n-2$ electrons and the t orbitals accommodate 4 electrons. There remain $2n-2$ 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 $(^1/_2\ n - 1)$ 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 e.v. for n odd or large and even but may be less than 1 e.v. for C_4. The energy for π-electron excitation will decrease from about 2 e.v. 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 $2n-2$ 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] (M.R.B.) 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.

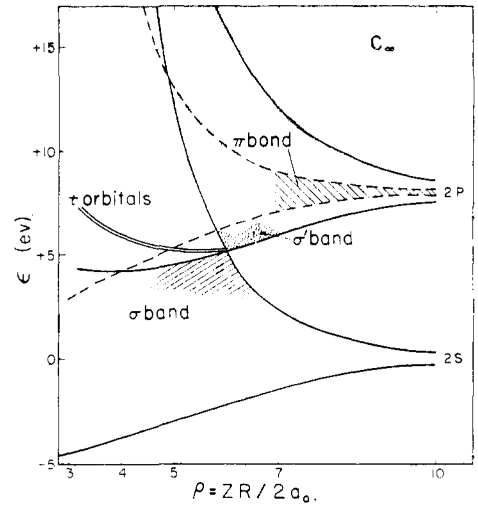

Fig. 4.—Electron orbital energy bands for long linear C_n. The curves marked t-orbitals are for the pair of orbitals associated primarily with the terminal carbon atoms.

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 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 $\Delta H_0{}^\circ$ for the formation of gaseous C_3 from each vapor pressure measurement. The value of $\Delta H_0{}^\circ$ is practically constant over the temperature range of Chupka and Inghram's measurements. The average is $\Delta H_0{}^0$ = 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 two or three kcal./mole or possibly even more.

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[14] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[15] A. Loftbus, *ibid.*, **79**, 24 (1957).

[16] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

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

The calculation of molecular orbital energies for C_n linear molecules is analogous to that for hydrocarbons with alternate single and double bonds. Assuming the molecular axis is in the z-direction, the two $2p_\pi$-orbitals for each atom point in the x- and y-directions (or the two π-orbitals may be taken to have ± 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

$$\beta_{ij} = \gamma_{ij} - {}^1\!/_2 S_{ij}(\alpha_{ii} + \alpha_{jj}) \tag{3}$$

also

$$x_{ij} = {}^1\!/_2(\alpha_{ii} + \alpha_{jj}) - \epsilon \tag{4}$$

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 $\alpha_{ii} = \alpha_0$ because all the C atoms have the same electronegativity.

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[18,19,20]

$$\epsilon_i = \beta_0 K_i = \beta_0 \left(2 \cos \frac{i\pi}{2n + 1}\right) \quad (i = 1, 2, \cdots, n) \tag{5}$$

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, the solutions of eq. 1 are of the form

$$\epsilon_i = \frac{K_i}{1 + SK_i}\, \beta_0 \tag{6}$$

The values for overlap integral at 1.28 Å. 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 Å. (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 Å. 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_0-values (and standard distances) are 44.5 kcal./mole (for 1.33 Å.), 81 kcal./mole (for 1.353 Å.) and 102 kcal./mole (for 1.353 Å.). Figure 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_0^0 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_0^0 of formation for C_3, the heat of formation for C_n is 186.5 plus $(n - 3)$ 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 0.7% of the heat of formation at C_{10}.

While there is a gradually increasing divergence between the three series of calculated values of ΔH_0 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.

TABLE I

CALCULATED VALUES FOR ΔH_0^0 OF FORMATION[a] (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

[a] For C(gas), C_2 and C_3, the observed value of ΔH_0^0 of formation are 169.58, 200 and 186.5 kcal./mole, respectively.

In addition to the results for molecules through C_{13} shown in Table I, ΔH_0^0 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./g. atom of carbon.

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 $-(F_T^0 - H_0^0)/T$ 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

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(18) E. Hückel, *Z. Physik*, **70**, 201 (1931); **76**, 628 (1932).

(19) J. E. Lennard-Jones and J. Turkevich, *Roy. Soc. Proc.* (*London*), **A158**, 280 (1937).

(20) C. A. Coulsen, *ibid.*, **A169**, 413 (1939).

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

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 most important is ν_2 where 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 ± 0.0005 cm.$^{-1}$ which corresponds to a C–C distance of 1.281 Å.

The best basis now available for estimating the increment to a thermodynamic function such as $-(F^0 - H_0^0)/T$ from C_n to C_{n+1} is one-half the difference in that function 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, $R \ln 6 = 3.56$ cal./deg. mole must be added to the $-(F^0 - H_0^0)/T$ and S_0 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 $-(F_T^0 - H_0^0)/T$ 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 $-(F^0 - H_0^0)/T$ and S^0 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.

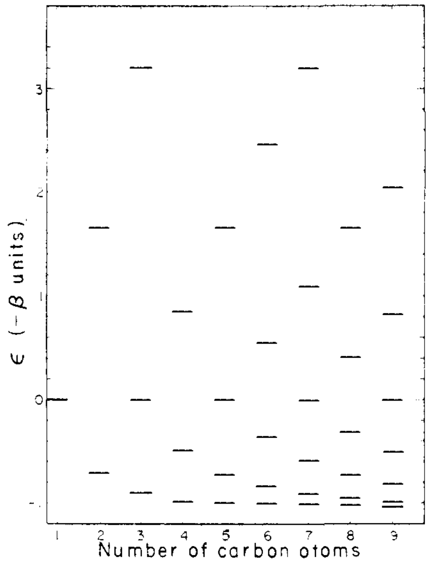

Fig. 5.—Calculated molecular orbital energies for linear molecules C_n.

TABLE II

THE FREE ENERGY FUNCTION[c] $-(F^0 - H_0^0)/T$ IN CAL./DEG. MOLE

Substance		T, °K. 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

Increment per carbon atom based upon C_3O_2. [b] Increment per carbon atom adjusted to triple point pressure. [c] 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 $(H^0 - H_0^0)/T$ 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	13.23	13.41
Increment per C atom	4.55	4.77	4.90	5.01	5.08

Calculated Vapor Pressures and Vapor Enthalpies.—By combination of the ΔH_0 of formation values with the $-(F_T^0 - H_0^0)/T$ 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

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[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).

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

[26] H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 937 (1951); R. L. Livingston and C. N. R. Rao, THIS JOURNAL, **81**, 285 (1959).

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 $-(F^0 - H_0^0)/T$ 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.

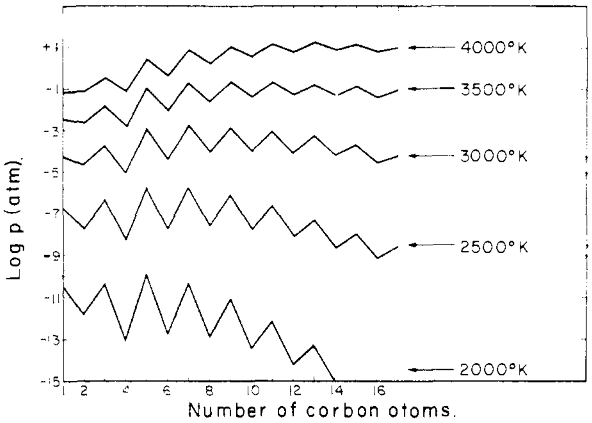

Fig. 6.—Calculated partial pressures of the various vapor species C_n in equilibrium with graphite at several temperatures.

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.

TABLE IV

THE ENTROPY[c] 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. [c] 3.56 cal./deg. mole is to be added to the values for even n species (except C_2), see text.

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 g. 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.

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./g. atom	H_T, kcal./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

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 species considered by the above authors. If we

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

denote this quantity by ΔH_{ap}, then for effusion experiments

$$\Delta H_{ap} = 169.5 - RT \ln \frac{\Sigma_n n^{1/2} P_n}{P_1} \qquad (7)$$

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 ΔH_{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 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 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 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 Bégué[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 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. While a $=C=C=C=C=$ 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 calculated readily for the ring by the same methods as for the chain. If $n = 4k + 2$ with 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 $(1800/n)$ 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, ±0.618, for C_{10} and ±2, ±1.802, ±1.247 and ±0.445 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

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

(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.

four electrons. The pattern of ring orbitals is repeated for the $2p_\pi$ orbitals perpendicular to the plane and for those radially oriented in the plane of the ring. Since ring strain was considered separately, we used the same β for both perpendicular and radial orbitals, and therefore the degeneracies stated above are doubled. The resulting ΔH_0^0 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 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 *difference* in the heats of formation derived from the temperature derivative of the abundances and (b) the *ratio* 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 e.v. in most cases.

TABLE VII

ELECTRON AFFINITY OF CARBON MOLECULES (E.V.)

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 e.v.

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° 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°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. g. atom at 4000°K. The heat of formation of liquid at 4000°K. is taken as the heat of formation per added carbon atom (given above for 0°K. and corrected to 4000°K.) of 11.4 kcal/g. atom less an estimated value of 1.0 kcal./g. 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./g. atom, at an interchain distance of 3.4 Å. corresponding 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./g. atom.

Now we have two estimates of the heat of fusion. From the energy calculations, $\Delta H_f = 10.4$ kcal./g. atom; but from the entropy calculations, $\Delta H_f = T\Delta S_f = 4000(16.82 - 14.18)/1000 = 10.5$ kcal./g. 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°K., which is 17.6 kcal./g. atom, and then by deducting the heat of fusion one obtains for the heat of vaporization of the liquid 7 kcal./g. 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.

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 than 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.

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

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 Å. 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 Å. (ethylene double bond) and a standard resonance integral $\beta_0 = -44.5$ 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_0 values are -81 and -102 kcal./mole for Slater orbitals or S.C.F. orbitals, respectively.

An additional correction of 0.5 β_0 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_0 coefficients and for conjugation energy are given in Table VIII.

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 $\Delta H_0{}^0$ of formation of the hypothetical C_n with localized bonds per interior carbon atom is then the difference in $\Delta H_0{}^0$ 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 Å. bond 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.

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	.444
(L-S)	Ethylene	1.275	...	1.508	1.048	.012
	Allene	1.277	0.845	1.432	0.710	.121
(L-F)	Ethylene	0.945	...	1.177	.718	.008
	Allene	0.946	0.770	1.140	.601	.098

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

The Method of Continuous Variations for Some Special Types of Reaction

BY MARK M. JONES

RECEIVED DECEMBER 29, 1958

An examination has been made of the use of the method of continuous variations for some types of reactions which do not follow the patterns already in the literature. The use of this method to establish the stoichiometry of complexes in solution is warranted in some cases where species are produced in addition to the complex. Its use is also warranted when one of the reactants or the complex is an acid or a base provided that certain restrictions are satisfied. The specific cases considered are: (1) where several species, in addition to the complex, are produced in stoichiometric amounts, (2) where the complex produced is a weak acid (or a weak base) and (3) where one of the reactants is the anion of a weak polyprotic acid or is a weak polybasic species. In many cases it is possible to establish the stoichiometry in a simple manner, while the evaluation of the stability constant of the complex cannot be accomplished using the simple equations given in the literature.

The use of the method of continuous variations (Job's Method) in studying complexes in solution is open to several objections and accompanied by restrictions of a fairly serious nature.[1-3] One of the most serious difficulties facing the prospective user of this method is a very fundamental one. This is the selection of a theoretical treatment from the literature which is based upon a prototype reaction that is similar to the reaction under study. In most cases this is simply not possible. The purpose of this paper is to show how this method may be used to establish the stoichiometry of complexes in some situations where the complex-forming reactions possess complicating features not previously considered. In all of the reactions examined here, only *one* complex may be formed. For some cases where more than one complex is formed, recourse to the methods presented by Vosburgh[2,4] and by Katzin[5] is possible.

The types of reaction considered in this paper are (1) a complex is formed with the concurrent production of an arbitrarily large number of other species, all formed in stoichiometric amounts; (2) a complex is produced which is a weak monobasic acid; and (3) one of the reactants is the anion of a weak acid or a very similar type of reaction in which one of the reactants is a weak base.

In the derivations given below the usual assumptions are made in setting the concentrations of the various species equal to their activities. A method of correcting for this has been given in a previous paper.[3] The cases given here represent reactions of types which previously have been

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(1) F. Woldbye, *Acta Chim. Scand.*, **9**, 299 (1955).

(2) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

(3) M. M. Jones and K. K. Innes, *J. Phys. Chem.*, **62**, 1005 (1958).

(4) R. K. Gould and W. C. Vosburgh, THIS JOURNAL, **64**, 1630 (1942).

(5) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5455, 5659 (1950).