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(Received June 7, 1948)

Earlier formulas for the electron-pair bonding energies of methane, and radicals derivable from methane, are combined with recent data on the energy levels of the carbon atom, the heat of sublimation of carbon, the energy for removal of the first hydrogen, and the dissociation energy of CH to obtain the energies of CH_3 and CH_2. A consistent set of values is found which is in agreement with a heat of sublimation of carbon of 120–140 kcal. and gives for the energies of successive removals of hydrogen atoms from methane 101, 90, 80, and 80 kcal., respectively.

IN an earlier paper[1] an extended Heitler-London-Pauling-Slater valence calculation was made for methane, following methods developed by J. H. Van Vleck,[1] and the relative energies of CH_4, CH_3, CH_2, and CH were computed, using certain experimental data to fix the values of the integrals occurring in the formulas for electron pair bonds. Subsequent new and more accurate experimental values are used in the present note to correct the computed energies and to obtain some information about the heat of sublimation of carbon. The new data now taken into account include a careful theoretical calculation of the term values of the carbon atom by Ufford,[2] the experimental location of the sp^3 ^5S state of carbon by Shenstone,[3] a more accurate value of the dissociation energy of CH given by Herzberg,[4] and the energy for the reaction $CH_4 = CH_3 + H$ from some recent experiments that are in good agreement.[5]

The procedure for utilizing this information is essentially the same as that followed before.[1] No changes have been made in the formulas for the energies according to the electron pair theory. The formulas are presumed to give the energies at the potential minima in the energy *versus* distance curves, and all energy values cited are for molecules at the potential minimum unless marked W_0

or otherwise noted. To obtain dissociation energies from the lowest vibrational levels, the zero point energies of Smith[6] are used. These are: CH, 0.18; CH_2, 0.46; CH_3, 0.82; and CH_4, 1.17 ev.

CARBON ATOM INTEGRALS

Of the integrals describing the carbon atom according to the Slater theory and for which numerical values are necessary in computing the valence energy, a minimum number are taken from the paper of Ufford[2] and the remainder are chosen to fit the known levels of the carbon atom. Since the Slater $F-G$ relationships (see ref. 1, Table II) cannot perfectly fit all the carbon levels, a selection is made which fits most closely those levels important in the quadrivalent state of carbon. The values employed are as follows, those from Ufford being averages for the excited and normal states.

Integral	Value, ev	Source
$F_0(2s, 2s)$	14.87 ⎫	
$F_0(2s, 2p)$	14.00 ⎬	Ufford
$F_0(2p, 2p)$	13.26 ⎭	
G_1	2.24 ⎫	To fit
F_2	0.21 ⎬	carbon
$I(2p) - I(2s)$	10.85 ⎭	levels

The carbon levels computed from these values are compared with the accurately known observed levels in Table I. Other selections for the carbon atom integrals were tried and were not found to give important differences in results for bond energies. The set listed above yields, for the valence state of carbon in methane, $W_v(C) = 6.97$ ev (see Eq. (21) of ref. 1). For plane CH_3 the

[1] H. H. Voge, J. Chem. Phys. **4**, 581 (1936). Also papers of J. H. Van Vleck referred to there.

[2] C. W. Ufford, Phys. Rev. **53**, 569 (1938).

[3] A. G. Shenstone, Phys. Rev. **72**, 411 (1947).

[4] G. Herzberg, *Molecular Spectra and Molecular Structure, I, Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939). The CH values were recomputed by Herzberg from observations of Shidei.

[5] D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942); G. B. Kistiakowsky and E. R. van Artsdalen, J. Chem. Phys. **12**, 469 (1944); H. C. Andersen and G. B. Kistiakowsky, J. Chem. Phys. **11**, 6 (1943); E. T. Butler and M. Polanyi, Trans. Farad. Soc. **39**, 19 (1943).

[6] L. G. Smith, Phys. Rev. **51**, 263 (1937).

valence state is

$$W_v'(C) = I(2p) - I(2s) - (1/6)[5F_0(2s, 2s) + 8F_0(2s, 2p) - 13F_0(2p, 2p) + G_1 + 29F_2]. \quad (1)$$

The above values lead to $W_v'(C) = 7.13$ ev.

RELATIVE ENERGIES OF CH$_2$ AND CH

The heat of dissociation, D_0, of CH is 3.47 ev,[4] and the zero point energy is 0.18, so that the energy of dissociation from the potential minimum is 3.65 ev. In the previous formula,

$$W(CH) - W(C) - W(H) = (3/2)F_2 + K(CH) + N_{ss} - N_{\sigma\sigma} + (1/2)N_{\pi\pi}, \quad (2)$$

substitution of -3.65 on the left, together with the values $N_{ss} = 2.0$, $N_{\sigma\sigma} = 2.3$, and $N_{\pi\pi} = -0.6$ ev, used throughout, leads to -3.36 for the quantity $K(CH)$. Then, from the formula for right-angled CH$_2$,

$$W(CH_2) - W(C) - 2W(H) = (3/2)F_2 + 2K(CH) + K(H_2) - (1/2)\beta + 2N_{ss} - 2N_{\sigma\sigma} + N_{\pi\pi} - 0.4, \quad (3)$$

where the -0.4 ev term is the correction necessary for an accurate solution of the secular equation in this case, and $K(H_2) - (1/2)\beta = 0.63$,[1] it is found that the energy necessary to dissociate CH$_2$ into atoms is 7.38 ev from the potential minimum, or 6.92 ev from the ground state.

RELATIVE ENERGIES OF CH$_4$ AND CH$_3$

Four alternative cases are considered: (a) that in which the heat of sublimation of carbon to s^2p^2 ^3P is considered to be 135.7 kcal. according to Hagstrum;[7] (b) the heat of sublimation is 125 kcal. according to Herzberg as quoted by Hagstrum;[7] (c) the heat for the reaction CH$_4$ = CH$_3$ + H is 101 kcal. from close values recently published;[5] and (d) the heat of sublimation is 170.4 kcal.[8] In cases (a), (b), and (d) the energy of formation of methane is calculated from experimental data and is used to evaluate the unknown integral $N_{s\sigma}$ in the theoretical formula for the energy, which then permits the energy of formation of CH$_3$ to be calculated. In case (c), $N_{s\sigma}$ is evaluated from the energy difference between methane and CH$_3$, and from it the energy of formation of methane and a value of the heat of sublimation of carbon, $L(C)$, is obtained. The formulas employed are

$$W(CH_4) - W(C) - 4W(H) = W_v(C) + 4K(CH_4) + 6K(H_2) - 3\beta + (1/2)N_{ss} - (5/2)N_{\sigma\sigma} - 3\sqrt{3}N_{s\sigma} + 4N_{\pi\pi}, \quad (4)$$

$$W(CH_3) - W(C) - 3W(H) = W_v'(C) + 3K(CH_4) + 3K(H_2) - (3/2)\beta - (3/2)N_{\sigma\sigma} - 3\sqrt{2}N_{s\sigma} + 3N_{\pi\pi}. \quad (5)$$

Here $K(CH_4) = -2.64$, and $K(H_2) - (1/2)\beta = 0.41$ for CH$_4$ and 0.34 for CH$_3$, from the Morse function for H$_2$.[1]

The method of computing the energy of formation of methane is as follows:

C(gr.) + 2H$_2$ = CH$_4$	$W_0(CH_4) - 2W_0(H_2) - W(C_{gr.})$	$= -0.69$ ev[9]
C(g) = C(gr.)	$W(C_{gr.}) - W(C)$	$= -L(C)$
4H = 2H$_2$	$2W_0(H_2) - 4W(H)$	$= -8.95$[4]
CH$_4$ = CH$_4$ (pot. min.)	$W(CH_4) - W_0(CH_4)$	$= -1.17$[6]
C(g) + 4H = CH$_4$ (pot. min.)	$W(CH_4) - W(C) - 4W(H)$	$= -10.81 - L(C)$

Results obtained are summarized below.

Case	a	b	c	d
$L(C)$, kcal.	(135.7)	(125)	126.5	(170.4)
$N_{s\sigma}$, ev	1.62	1.53	1.54	1.91
$W(CH_4) - 4W(H) - W(C)$, ev	-16.70	-16.23	-16.29	-18.20
$W(CH_3) - 3W(H) - W(C)$, ev	-11.88	-11.51	-11.56	-13.12

[7] H. D. Hagstrum, Phys. Rev. **72**, 947 (1947).
[8] L. Brewer, P. W. Gilles, and F. A. Jenkins, paper presented before American Chemical Society meeting, Chicago, April, 1948.
[9] $\Delta H^0_0 = -15.99$ kcal., D. D. Wagman et al., J. Res. Nat. Bur. Stand. **34**, 143 (1945).

TABLE I. Energy levels of the carbon atom, above $s^2p^2\ {}^3P$, in electron volts.

State	Observed	Computed
$sp^3\ {}^3S$	13.10[b]	13.12
${}^3P$	9.32[b]	9.55
${}^3D$	7.95[b]	8.29
${}^5S$	4.16[a]	4.16
$s^2p^2\ {}^1S$	2.68[a]	3.15
${}^1D$	1.26[b]	1.26
${}^3P$	0.00	0.00

[a] (See reference 3.)
[b] Edlen, quoted by Ufford (see reference 2).

The result in case (c) indicates a value of $L(C)$ in the neighborhood of 120 to 140 kcal. but cannot with certainty exclude $L(C) = 170.4$. A similar line of reasoning was set forth by Long and Norrish[10] as an argument in favor of $L(C) = 125$ kcal.

HEATS OF REMOVAL OF HYDROGEN ATOMS

Heats necessary for the removal of successive hydrogen atoms from methane, according to the cases outlined above, are summarized in Table II. These heats are, of course, computed from the lowest vibrational states and not from potential minima. The average bond energies—namely, one-fourth the heat required to remove all four hydrogen atoms—are: (a) 89.6, (b) 86.8, (c) 87.2, and (d) 98.2 kcal. The individual bond strengths differ considerably from the averages. Within the accuracy of this method of calculation, in the first three cases the heats of removal of successive hydrogens from methane are 101, 90, 80, and 80 kcal., respectively. This is the most significant result of calculations such as the present. There is no evidence that CH_3 will part with a hydrogen atom more readily than the other radicals, although this has often been suggested because the carbon atom drops down into the divalent s^2p^2 state in this step. The explanation for the absence of such an effect is, of course, that intrinsically stronger bonds are formed by sp^3 carbon and that these more than compensate for

TABLE II. Heats of removal of hydrogen atoms from methane and radicals, in kcal.

Process	(a) $L(C) = 135.7$	(b) $L(C) = 125$	(c) $W_0(CH_2) - W_0(CH_4) + W(H) = 101$	(d) $L(C) = 170.4$
$CH_4 = CH_3 + H$	103.1	100.8	(101.0)	109.1
$CH_3 = CH_2 + H$	95.5	86.9	88.1	124.0
$CH_2 = CH + H$	79.6	79.6	79.6	79.6
$CH = C + H$	(80.0)	(80.0)	(80.0)	(80.0)

the necessary promotional energy of the carbon atom. It may be noted, however, that no effort is made here to evaluate the intrinsic bond strengths corresponding to a process in which hydrogens are removed while the state of the carbon remains unchanged, because these are not at present measurable or useful quantities. The attempt of Long and Norrish[10] to express bond energies in terms of the heat of sublimation of carbon to the $sp^3\ {}^5S$ state does not appear to be helpful since the ${}^5S$ state is not observed as a metastable product; their attempt also disagrees with calculations of the present type which show that the ${}^5S$ level does not properly measure the energy of the carbon atom in the quadrivalent state.

It is pointed out by Stevenson[11] that the present values for the relative energies of CH_4 and CH_2 in cases (a), (b), and (c) are in good agreement with the following estimates from electron impact data.

Process	Energy, ev	Reference
$CH_4 = CH_2^+ + H_2$	15.7 ±0.5	Smith[6]
$H_2 = 2H$	4.48	Herzberg[4]
$CH_2^+ = CH_2$	−11.9 ±0.2	Langer and Hipple[12]
$CH_4 = CH_2 + 2H$	8.28	

For the same process in cases (a), (b), and (c) the computed energies are 8.61, 8.14, and 8.20 ev, respectively. For case (d) the computed value is 10.11 ev, and the disagreement of this with 8.28 ev may also be taken as evidence against $L(C) = 170.4$ kcal.

[10] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. A187, 337 (1946).

[11] D. P. Stevenson, these laboratories, private communication.
[12] A. Langer and J. A. Hipple, Phys. Rev. 69, 691 (1946).