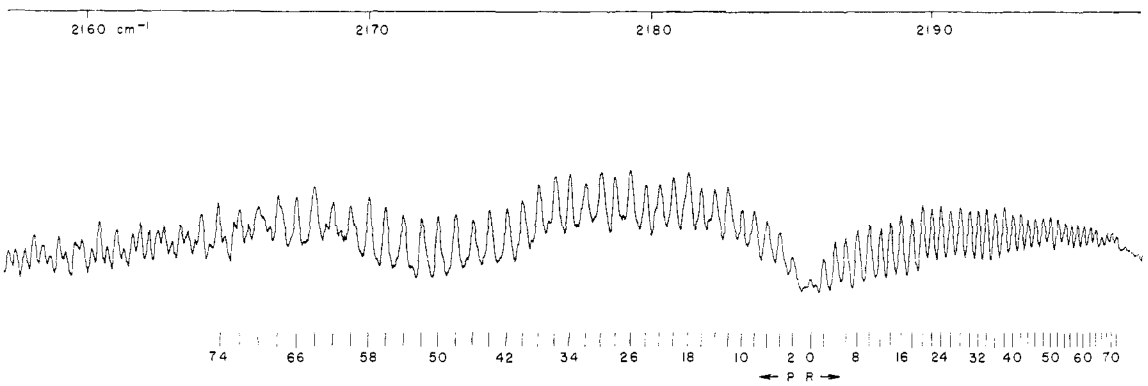

Fig. 1.—The $\nu_1 + \nu_3$ band of CS_2 with center at 2185.52 cm.$^{-1}$. The P branch is overlapped by another band. The cell length was 1 meter and the pressure was 3 cm.

data are sufficient to determine the bond distances in these two molecules. The B_0 value of O^{16}-$C^{12}S^{32}$ has also been determined from infrared measurements but does not provide sufficient information to determine the two bond distances in the molecule. Fortunately, microwave values are available for several isotopic species of OCS. Unfortunately, zero-point energies vary enough among the isotopic species to give several values of the bond distances depending on which pair of B_0 values are used to evaluate these parameters. Since the carbon atom will be fairly close to the center of mass the isotopic pair O^{16}–C^{12}–S^{32} and O^{16}–C^{13}–S^{32} seem to be the most appropriate pair to use in evaluating r_{CO} and r_{CS}. This is borne out by the fact that the B_0 values are very nearly equal. Thus using this pair of B_0 values and the B_0 values of CO_2 and CS_2 determined from the infrared work, the bond distances for the three molecules have been calculated. These values are compared in Table III. It is readily seen that within experimental error the C–O distance in CO_2 and OCS are the same. The same is true of the C–S distance in CS_2 and OCS.

TABLE III

COMPARISON OF BOND LENGTHS IN CO_2, OCS AND CS_2

Molecule	r_{CO}	r_{CS}
CO_2	1.162	
OCS	1.163	1.559
CS_2		1.553

Acknowledgment.—In conclusion the authors wish to thank Joseph M. Cameron and Carroll Dannemiller for carrying out the least square reduction of the data on SEAC.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Electronic Correlation in Molecules. III. The Paraffin Hydrocarbons[1]

BY KENNETH S. PITZER AND EDWARD CATALANO

RECEIVED MAY 31, 1956

It is shown that the isomerization energy of paraffin hydrocarbons arises principally from an electronic correlation effect. The dispersion force formulation, which corresponds to the dipole–dipole approximation, is used for interactions between all pairs of non-adjacent atoms in the molecule and an expression for the total electronic correlation energy between non-adjacent atoms is given. The theoretical isomerization energies for the butanes and pentanes agree quite satisfactorily with observed values. By use of empirical values for C–C and C–H bond energies a general expression for ΔH_f° at 0°K. for the paraffin hydrocarbons is also presented.

In a brief note[2] one of us has pointed out that the anomalous trend in dissociation energy for the halogen series is at least partially explained by the correlation energy of the unshared pairs of electrons or in other words the London or dispersion energy. The trend in polarizability of the halogens shows an abrupt drop from chlorine to fluorine and this leads to a great reduction in correlation energy. In this paper, we report calculations which show that the isomerization energies for the paraffin hydrocarbons arise principally from the same electron correlation effect.

We note that several completely empirical treatments for the correlation of the isomerization energies have been made and are quite satisfactory.[3]

We realize that electrostatic interactions of the time average charge distribution also may be significant. However, the information necessary for a quantitative calculation is not available, and the paraffins are known to be relatively non-polar.

In these calculations, we assume that the C–C

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(1) This research was assisted by the American Petroleum Institute through Research Project 50.

(2) K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

(3) J. R. Platt, *J. Phys. Chem.*, **56**, 328 (1952); K. Ito, THIS JOURNAL, **75**, 2430 (1953).

and C–H bond energies are constant and consider only electron correlation effects between atoms not directly bonded to one another. We use the polarizabilities given by Ketelaar[4]: $\alpha = 0.42$ and 0.93×10^{-24} cm.^{3} for hydrogen and carbon atoms, respectively. These values satisfactorily reproduce the observed polarizabilities of light hydrocarbons. The correlation energies were calculated by the variation method formula of Slater and Kirkwood[5]

$$\Delta E_{\mathrm{AB}} = -\frac{3e\hbar}{2m^{1/2}R^6} \cdot \frac{\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}}{[(\alpha_{\mathrm{A}}/N_{\mathrm{A}})^{1/2} + (\alpha_{\mathrm{B}}/N_{\mathrm{B}})^{1/2}]} \quad (1)$$

where the numbers of polarizable electrons, N_{A}, N_{B}, were taken as one and four for hydrogen and carbon, respectively. Equation 1 applies to a pair of atoms and the necessary number of terms must be taken to include the desired interactions. The following formula results

$$\Delta E_{\mathrm{c}} = -\,[22.6\Sigma R_{\mathrm{CC}}^{-6} + 8.68\ \Sigma R_{\mathrm{CH}}^{-6} + 3.42\Sigma R_{\mathrm{HH}}^{-6}] \times 10^{-60} \text{ ergs} \quad (2)$$

where the sums are over all of the interatomic distances of the types indicated.

The results of Paper II indicate the selection of equation 2 but we may check the correctness of this formula independently by the intermolecular potential for a pair of methane molecules. At a distance of 4.27 Å. between molecular centers, which is the location of the van der Waals potential minimum, the calculated energy is 3.8×10^{-14} ergs. This was obtained by summing over all C–C, C–H and H–H terms between the two molecules. The Lennard-Jones potential which yields agreement with the experimental second virial coefficient of methane has the parameters[6] $\epsilon/k = 145°$ and $r_0 = 4.27$ Å. The corresponding energy contribution of the inverse sixth power term is 4.0×10^{-14} ergs. The agreement within 5% is certainly fortuitous, but it offers strong support for the approximate correctness of equation 2.

TABLE I

INTERNAL ENERGIES OF THE PARAFFIN HYDROCARBONS (KCAL./MOLE)

Substance	Conformation	$-\Delta E_{\mathrm{c}}$	$-\Delta H_{\mathrm{f}}$ calcd. (°K.) (a)[b]	(b)[b]	$-\Delta H_{\mathrm{f}}$[c] (°K.) obsd.
Methane	.....	8.80	14.31	14.98	15.99
Ethane	.....	17.35	16.50	16.46	16.52
Propane	.....	27.24	20.03	20.03	19.48
n-Butane	*trans*	37.20	23.63	23.63	23.67
n-Butane	*gauche*[a]	39.12	23.05	...	22.87
Isobutane	.....	38.48	24.91	25.15	25.30
n-Pentane	*t-t*	47.16	27.23	27.23	27.23
n-Pentane	*t-g*[a]	49.18	26.75	...	26.73
Isopentane[a]	.....	50.46	28.03	28.74	28.81
Neopentane	.....	50.99	31.06	32.08	31.30
Δ per CH_2 for *n-trans*		9.96	3.60	3.60	3.64

[a] The calculated ΔH_{f} for these cases include a strain energy correction—see text. [b] (a) calculated ΔH_{f} using zero point energy obtained from equation 3—see text, (b) calculated ΔH_{f} using observed zero point energy data. [c] Estimated error in experimental $\Delta H_{\mathrm{f}} \pm 0.2$ kcal./mole.

Table I summarizes the calculated energy terms for the paraffins through the pentanes. $-\Delta E_{\mathrm{c}}$ is the electronic correlation energy between atoms not directly bonded to one another. Since the C–C and C–H bond energies and bond distances are assumed to be constant, the inclusion of correlation energies for the bonds would not affect the final results. Tetrahedral bond angles and staggered torsional orientations are taken throughout. The bond distances assumed are (C–C) = 1.54 Å. and (C–H) = 1.10 Å.

Since the zero point vibrational energy is an extraneous effect, the changes in total zero point vibrational energy were taken into account wherever the necessary data exist. The sums of vibrational frequencies, multiplied by $^1/_2h$ are given in Table II. The frequency values come from several sources.[7] Since the complete sets of frequencies are not available in some cases, an empirical equation was developed.

$$^1/_2h \sum_{i} \nu_i = (17.70n + 9.82) \text{ kcal./mole} \quad (3)$$

Here n is the number of carbon atoms. The values resulting from equation 3 are also shown in Table II.

TABLE II

ZERO POINT ENERGY OF VIBRATION IN KCAL. PER MOLE

Substance	$\frac{1}{2}h\Sigma\nu_i$	Eq. 3	Difference
Methane	26.85	27.52	0.67
Ethane	45.26	45.22	− .04
Propane	62.92	62.92	.00
n-Butane	80.62	80.62	.00
Isobutane	80.38	80.62	.24
n-Pentane	98.32	98.32	.00
Isopentane	97.61	98.32	.71
Neopentane	97.30	98.32	1.02
Δ per CH_2	17.70	17.70	.00

The last column in Table I lists the observed[8] heats of formation corrected to 0°K. By adjustment of the values assumed for the C–C and C–H bond energies the following equation is obtained

$$\Delta H_{\mathrm{f}}\,(0°\mathrm{K.}) = -11.34n - 21.69 + \Delta E_{\mathrm{c}} + \Delta E_{\mathrm{s}} + \frac{1}{2}h\sum_{i}\nu_i \quad (4)$$

n is the number of carbon atoms. ΔE_{s} is a term to be included if there is significant steric repulsion between non-bonded atoms. It is zero except in a few cases to be discussed below.

If the first two terms in equation 4 are rearranged into C–C and C–H bond energies, one obtains the values 80.2 and 102.4 kcal./mole, respectively. These values were obtained using the heat of sublimation of carbon into atoms as 170 kcal./

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(4) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Pub. Co., Amsterdam and Houston, 1953, p. 90.

(5) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

(6) These parameters are the mean of concordant values reported by H. S. Taylor and S. Glasstone, "A Treatise on Physical Chemistry," 3rd ed., Vol. 2, D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 328.

(7) Frequencies quoted or estimated and references given in: G. H. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, pp. 307, 344, 361; W. B. Person and G. C. Pimentel, THIS JOURNAL, **75**, 532 (1953); K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940), *Chem. Revs.*, **27**, 39 (1940), *Ind. Eng. Chem.*, **36**, 829 (1944).

(8) All observed values except for gauche conformations from American Petr. Inst. Res. Proj. 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, Table 20w. Values for gauche modifications obtained from data presented in: W. B. Person and G. C. Pimentel, THIS JOURNAL, **75**, 532 (1953); N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 86 (1949); K. S. Pitzer, *ibid.*, **8**, 711 (1940).

mole and the dissociation energy of hydrogen as 103.2 kcal./mole, both at 0°K. These bond energies, however, are not the proper ones to use for normal thermochemical calculations unless electron correlation, strain and zero point energies are used throughout. Bond energies as calculated without the inclusion of the dispersion forces and zero point energies are[9] 80.5 and 98.2 kcal./mole for C–C and C–H, respectively. In the calculations of bond energies, it will be noted that the zero point energy almost compensates the dispersion energy yielding bond energies which do not differ greatly from those calculated in the usual manner.

It should be emphasized that there are the same number of C–C and C–H bonds in isomeric hydrocarbons. Consequently, the empirical adjustment of these bond energies in no way affects the isomerization energies. For the *iso*- to *n*-butane isomerization the observed ΔH is 1.63 kcal./mole and the calculated value, considering zero point energy differences, is 1.50. In the case of *neo*- to *n*-pentane the observed ΔH is 4.07 and the calculated value is 4.85 kcal./mole. These agreements are quite satisfactory in view of possible experimental errors and theoretical approximations. In judging the accuracy of these comparisons it should be remembered that the total dissociation energy of a pentane is approximately 1500 kcal./mole.

It has long been known that the skew or *gauche* conformation of *n*-butane or a larger paraffin involves a significant repulsive strain between two hydrogen atoms which are brought close together. The net increase in energy over the all *trans* conformation has been found to lie in the range of 0.5–0.8 kcal./mole.[10] When the attraction arising from electron correlation is taken into account, the repulsive strain energy term becomes 2.50 kcal./mole. This value yields practically perfect agreement for the energy difference between *trans–trans* and *trans–gauche* for *n*-pentane and satisfactory agreement for *gauche* *n*-butane. Unfortunately the zero point energy is not known precisely for the *gauche* conformations and must be estimated to be equal to that of *trans* conformations. This same strain energy appears in isopentane and when it is appropriately considered, the theoretical energy is in excellent agreement with the observed value.

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[9] K. S. Pitzer, "Quantum Chemistry," Prentice–Hall, Inc., New York, N. Y., 1953, p. 170.

[10] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949); S. Mizushima, "Structure of Molecules," Academic Press, Inc., New York, N. Y., 1954, p. 98 f.

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heats of Formation of Sodium Molybdate, Molybdic Acid and Aqueous Molybdate Ion

BY ROBERT L. GRAHAM AND LOREN G. HEPLER

RECEIVED MAY 7, 1956

The construction of a calorimeter for the measurement of heats of solution has been described. Heats of solution of H_2MoO_4, MoO_3 and Na_2MoO_4 have been determined in various solutions. From these data we have calculated the heats of formation of H_2MoO_4(c), Na_2MoO_4(c) and $MoO_4^{=}$(aq) to be, respectively, −249.9, −350.4 and −238.2 kcal./mole. The free energy of $MoO_4^{=}$(aq) has been calculated to be −201.8 kcal./mole and the standard oxidation potential of the Mo/$MoO_4^{=}$ couple calculated to be 0.92 v.

In connection with the determination of the heat of formation of several slightly soluble molybdates it became desirable to have a reliable value for the heat of formation of sodium molybdate and aqueous molybdate ion. A search of the literature indicated that the reported values for these heats of formation might not be entirely reliable and that the whole problem could profitably be reinvestigated. A series of exploratory calorimetric determinations of the heats of solution of molybdic acid, molybdic oxide and sodium molybdate gave rough values for the various heats of formation that were considerably different from those tabulated by the Bureau of Standards[1] and Bichowsky and Rossini.[2] In order to resolve these discrepancies a series of careful calorimetric determinations was undertaken.

Experimental

The calorimeter consists of a Pyrex vacuum flask, specially built without spacers, and an evacuated stopper which fit together by means of a ground glass joint. Electrical leads and the calorimeter stirrer pass through a small glass tube in the stopper. The stopper is permanently fastened to the underside of the lid of the constant temperature bath so that while the calorimeter is in operation it is completely below the surface of the water in the bath. During a calorimetric run the temperature in the bath is controlled to within 0.003°. The flask is of such size that it holds 950 ml. of solution with a very small space above the surface of the liquid which minimizes the opportunity for evaporation. The sample is contained in a thin-walled glass bulb which is taped and waxed to the bottom of the stirrer. The stirrer shaft is so arranged that we can slide it down and break the sample bulb on the bottom of the flask. There is a propeller immediately above the sample bulb to aid in effecting rapid solution when the sample bulb is broken. The stirrer shaft is driven by a small synchronous motor.

A resistance thermometer consisting of about 45 ohms of no. 40 nylon insulated copper wire and a heater of about 120 ohms of no. 40 enameled manganin wire are contained in a closely wound glass coil made of 6 mm. Pyrex tubing and filled with HyVac oil. The coil also serves as a stirring well. The heater and thermometer wires were wound bifilarly on small metal rods in order to get the wires into a coil suitable for introduction into the glass coil. With the aid of an aspirator the heater wire was introduced into the bottom part of the glass coil and the thermometer into the top. Leads to the heater are of no. 24 copper wire and the leads to the thermometer are no. 24 manganin wire.

Resistance changes of the thermometer are determined

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[1] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

[2] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.