The Heats of Combustion of Acenaphthene, Acenaphthylene, and Fluoranthene. Strain and Delocalization in Bridged Naphthalenes

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The heats of formation of solid and gaseous acenaphthene, acenaphthylene, and fluoranthene have been determined via their heats of combustion and their heats of vaporization. The heats of combustion were determined in an aneroid oxygen bomb calorimeter. A simplified method of calculating the gas compression term in the correction of the heat of combustion to standard states is presented. The heats of vaporization were derived from vapor pressure curves determined by an effusion cell technique. Thermochemical stabilization energies relative to appropriate reference structures indicate that in acenaphthene the bridging ring is strained to the extent of 6–7 kcal. mole^{-1}; in acenaphthylene the bridging ring strain is nearly balanced by the stabilizing interaction of the double bond with the naphthalene nucleus with a net strain of ~2 kcal. mole^{-1}; in fluoranthene the ring strain predominates and there is a net strain of 6–7 kcal. mole^{-1}.

Introduction

The nature and extent of aromaticity in polynuclear aromatic hydrocarbons has been a subject of considerable interest in organic chemistry. Acenaphthylene (I) and fluoranthene (II) are two well-known aromatics
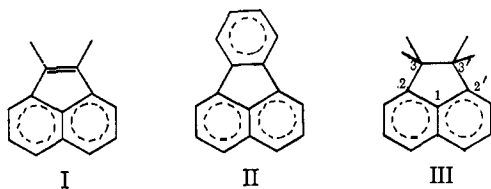
in which the formal possibility exists of delocalization between a bridging π-electron system and the naphthalene nucleus. Hückel molecular orbital calculations (HMO) indicate an additional delocalization energy of 0.94 and 0.82β[1] over that of the naphthalene and naphthalene and benzene systems, respectively. These molecules also satisfy Craig's rules.[2] However, HMO calculations usually overestimate such effects. Furthermore their perimeters are not $4n + 2$ alternate π-systems and these molecules have to be considered as separate naphthalene and ethylene and benzene systems, respectively, to conform to this rule.[3] In addition, the five-membered rings formed by the bridging groups should be strained to some extent. The purpose of the present work was to undertake a thermochemical study of the relative effects of the electronic interaction

and strain. Acenaphthene (III) has also been included to study the pure strain effect in the bridging ring.

Experimental Methods and Results

1. Combustion Calorimeter. The heat of combustion calorimeter (see Figure 1) is an aneroid rotating bomb type, similar to that of Keith and Mackle.[4] It differs in that the isothermal jacket (1) and rotation carriage (2) are immersed in a thermostated water bath ($\pm0.001°$) rather than in an air thermostat. The rotation mechanism is similar in mechanical principle to the bomb drive of the calorimeter of Hubbard, Katz, and Waddington.[5] Rotation about two axes is achieved by a single shaft. The large gear (3) around the jacket is mounted on a ball bearing race (4) in which the jacket is free to rotate. The small bevel gear (5) driving the large gear is free to turn on the drive shaft, but in one direction of motion is locked to the carriage stand by means of a rachet (6). The over-all rotation of the bomb is then achieved by means of rocking motion which advances the jacket in the ball race in one direction only. The gears and jacket, inside and out, are nickel plated to avoid corrosion and to reduce radiative heat transfer between the bomb and the jacket.

The bomb is (7) machined from a piece of 4-in., round, pure copper stock and has an interior volume of 125 ml. The resistance thermometer is wound noninductively into grooves (8) in the bomb from no. 30 gauge enameled copper thermocouple wire and has a resistance of approximately 25.5 ohms at 25° with a temperature coefficient of approximately 0.100 ohm/°C. The interior of the bomb and bomb lid (9) are lined with 0.010-in. platinum. All exposed interior fittings are of pure platinum. The lid is equipped with a single valve (10) for admitting and releasing oxygen which uses the parts for the valve on the Parr Instrument Co. 1105 oxygen bomb. The insulated electrode (11) is a Parr Instrument Co. A277A electrode assembly. The sample holder (12) is a platinum crucible that hangs from stirrups attached to the insulated electrode. The crucible swings in the stirrups in one direction of rotation so that the bomb may be inverted after filling. In the other direction of rotation the crucible falls from the stirrups to permit washing during bomb rotation. The crucible is also fitted with a conical baffle suspended over the top as a partial lid. The sample pellet is placed in the crucible over a cotton thread, 2.75 in. long, leading to a no. 36 gauge platinum ignition wire (13) stretched between the insulated electrode and the oxygen filling tube. The ignition system and the measurement of the ignition energy has been previously

(1) A. Pullman and B. Pullman "Les Theories electroniques de la chemie organique," Masson et Cie, Paris, 1952.

(2) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(3) For a discussion of aromaticity, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(4) W. A. Keith and H. Mackle, *Trans. Faraday Soc.*, **54**, 353 (1958).

(5) W. N. Hubbard, C. Katz, and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

described.[6] The heat of combustion of the cotton thread was determined in separate experiments.

The resistance thermometer is connected to the resistance bridge by a three-wire connection (single potential lead). All materials in the connections as far as the bridge are of copper to avoid thermal e.m.f. generation. The resistance bridge is a modified G-1 Mueller-type (Rubicon Instrument Co. Catalog No. 1551). It was modified by placing in an insulated box maintained at 35° by air circulated from another chamber with a blower and controlled heater. The top of the bridge box is made of Plexiglas and the resistance dial shafts are extended through the lid by means of nylon rod extensions. The bridge unbalance is detected by a Liston-Becker breaker-type amplifier (Beckman Instrument Co. Model 14). The output of the amplifier is fed to a strip chart recorder (Leeds and Northrup Co. Model H. Azar). Temperature vs. time curves are taken in the manner described by Jessup,[7] except that the bridge unbalance and times are read from the strip chart after the experiment. Noise levels are such that temperature changes corresponding to 0.00005° can be detected. Corrected temperature rises in ohms were calculated from temperature vs. time curves by numerical integration of the heat-flow equation.[8] The calculation is carried out by means of a digital computer.

Oxygen is purified by the method described by Jessup.[7] Combustions were carried out at 31 atm. of oxygen pressure.

Samples are weighed to 1 μg. on a Mettler Model M5 S/A microbalance.

For the compounds studied in this work the rotation feature of the apparatus is not necessary and the bomb was used in static position.

The energy equivalent of the calorimeter was established by combustion of benzoic acid (National Bureau of Standards Sample 39h). During calibration runs 0.37 ml. of water was added to the bomb to conform with the National Bureau of Standards recommended ratio of bomb volume to water. In runs on the compounds studied, the water volume was reduced to 0.10 ml. The average energy equivalent of the calorimeter without contents as determined from six calibrations is 8972.2 cal. ohm^{-1} with a standard deviation of 2.8 cal. ohm^{-1}.

2. Effusion Cell Technique. The effusion cell technique used is similar to that of Swan and Mack.[9] The cell is an aluminum cup (approximately 20 mm. i.d.) with a lid that consists of an aluminum annulus with a Teflon washer that screws on to the top of the cup. A piece of aluminum foil with the effusion hole in it is held over the cup by the lid. In use, the cup rests on a copper plate, silver soldered to a 2-in. diameter by 3-in. long copper-to-glass seal which in turn is connected to a high-vacuum line. The copper portion is immersed in a water or oil bath for temperature control. This arrangement provides excellent heat transfer to the effusing compound which is an essential considera-
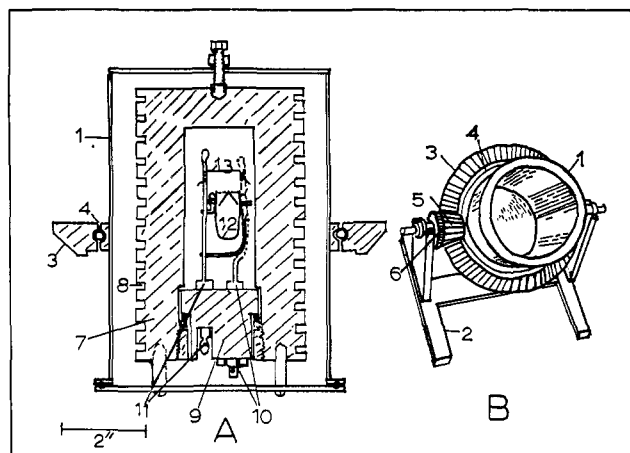

Figure 1. Aneroid rotating bomb calorimeter: A, cross section of bomb and jacket; B, elevation of rotation carriage and jacket.

tion in effusion cell work. The effusion hole diameter used in the present work was 0.333 mm. as measured by a microscope with a calibrated reticule. The average foil thickness was 0.025 mm. with the edge of the hole sharpened by polishing with fine abrasive paper. The Clausing factor should be ≥0.96 and was taken to be unity.

3. Samples Used. Acenaphthylene was purchased from K & K Laboratories and was purified by the following procedure. The picrate was formed in (1:1) benzene–ethanol and recrystallized from (1:1) toluene–ethanol. It was decomposed from suspension in benzene with aqueous ammonium hydroxide. The washed and concentrated solution in benzene was chromatographed through alumina and eluted with benzene. The reconcentrated solution was added to light petroleum from which the acenaphthylene precipitated. It was then recrystallized several times from light petroleum. This material was then sublimed twice along a temperature gradient and the center fraction was kept. The final melting point was 93.0–93.5°.

Acenaphthene was from the Matheson Co. It was purified by recrystallization several times from ethanol and sublimed twice along a temperature gradient and the center fraction was kept. No impurities were detected by g.l.c. from benzene solution with a silicone oil on firebrick column.

Fluoranthene was Purissma grade purchased from the Aldrich Chemical Co. It was purified by sublimation twice along a temperature gradient and the center fraction kept.

4. Results. The energy of the isothermal bomb process was corrected to standard states by the method described in the Appendix. Sample weights were reduced to *vacuo* using the following densities: acenaphthylene, 1.2 g. ml.$^{-1}$ (estimated); acenaphthene, 1.22 g. ml.$^{-1}$ [10]; fluoranthene, 1.238 g. ml.$^{-1}$.[11] The resulting energies of combustion *per* gram at standard states and 25° are listed in Table I.

The vapor pressures were fitted to an equation of the form $\log P = A/T + B$ by least squares. The A and B constants are listed in Table II. Heats of vaporization were determined from this equation by means of the

(6) R. H. Boyd, *Rev. Sci. Instr.*, **35**, 1086 (1964).
(7) R. S. Jessup, National Bureau of Standards Monograph No. 7, U. S. Government Printing Office, Washington, D. C, Feb. 26, 1960.
(8) W. N. Hubbard, D. W. Scott, and G. Waddington in "Experimental Thermochemistry," Vol. I, F. D. Rossini, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 5.
(9) T. H. Swan and E. Mack, Jr., *J. Am. Chem. Soc.*, **47**, 2112 (1925).

(10) H. W. W. Ehrlich, *Acta Cryst.*, **10**, 699 (1957).
(11) S. C. Chakravarti, *ibid.*, **7**, 378 (1954).

Table I. Energy of Combustion at 25°

m^a	$m_F{}^b$	ΔR^c	$\Delta R'^d$	$q_1{}^e$	$q_2{}^f$	$q_3{}^g$	$-\Delta E_c°$ (cal./g. air vs. ss)^h
			Acenaphthene				
0.188654	0.002055	0.203923	0.202973	0.89	0.62	0.91	9641.3
0.172761	0.002211	0.186772	0.185750	0.89	0.58	0.91	9634.4
0.181559	0.002198	0.196402	0.195386	0.89	0.58	0.91	9643.5
0.183152	0.002133	0.198046	0.197060	0.89	0.65	0.91	9641.2
0.183154	0.002281	0.198118	0.197064	0.89	0.66	0.91	9641.2
							9640.3 Av.
							$\sigma = 3.1$
							9633.5 (cal./g. vac.)
			Acenaphthylene				
0.186539	0.002174	0.198950	0.197945	0.94	0.66	1.00	9506.8
0.185644	0.002237	0.198093	0.197059	1.00	0.65	1.00	9509.6
0.186149	0.002234	0.198557	0.197524	1.00	0.69	1.00	9506.0
0.184693	0.002162	0.197100	0.196101	1.00	0.62	1.00	9512.2
0.192326	0.002188	0.204788	0.203776	0.89	0.76	1.00	9493.4
0.182380	0.002153	0.194364	0.193368	0.89	0.44	1.00	9501.1
							9504.8 Av.
							$\sigma = 6.5$
							9497.7 (cal./g. vac.)
			Fluoranthene				
0.187332	0.002285	0.196641	0.195584	1.37	1.20	1.04	9349.5
0.191360	0.001808	0.200887	0.200051	0.87	0.93	1.04	9365.9
0.190776	0.002176	0.200282	0.199276	0.90	1.44	1.04	9355.2
0.191115	0.002002	0.200654	0.199728	0.79	1.08	1.04	9362.3
0.190078	0.002222	0.199436	0.198409	0.68	0.99	1.04	9352.2
0.189963	0.001962	0.199222	0.198315	0.74	1.20	1.04	9352.0
							9356.2 Av.
							$\sigma = 6.0$
							9349.8 (cal./g. vac.)

^{a} m = mass of sample (g. in air vs. ss). ^{b} m_F = mass of cotton thread fuse (g. in air vs. ss). ^{c} ΔR = corrected temperature rise (ohms). ^{d} $\Delta R' = \Delta R - m_F(0.4624)$ (ohms). ^{e} q_1 = electrical ignition energy (cal.). ^{f} q_2 = nitric acid correction (cal.). ^{g} q_3 = correction to standard states (Washburn correction) (cal.) ^{h} $-\Delta E_1° = [\mathcal{E}\Delta R' - q_1 - q_2 - q_3]/m$; the energy of combustion corrected to standard states. $\mathcal{E}$ = 8973.2 cal. ohm^{-1}, all determinations except first four for acenaphthylene for which ϵ = 8972.2 cal. ohm^{-1} due to slightly different bomb contents.

Table II. Vapor Pressures

Acenaphthene Temp., °C.	P, μ	Acenaphthylene Temp., °C.	P, μ	Fluoranthene Temp., °C.	P, μ
17.47	1.03	13.02	2.56	55.85	0.650
25.00	2.50	20.03	4.77	57.85	0.762
32.85	6.07	29.60	13.1	60.85	0.877
41.0	15.23	39.50	30.2	62.8	1.32
50.0	36.2	45.00	51.1	65.8	1.74
				70.2	2.91
				74.1	4.64
				78.5	6.85
				80.4	7.42

$\log P (\mu) = A/T(°K.) + B$					
A	B	A	B	A	B
−4496	15.481	−3714	13.375	−5332	12.983

Clausius–Clapeyron relation as

$$\Delta H_{vap} = -2.303RA \qquad (1)$$

Under the conditions of low pressure and the temperature range covering 25° for acenaphthylene and acenaphthene eq. 1 is accurate. For fluoranthene the temperature range lies slightly outside 25°.

Heats of combustion *per* mole and heats of formation are listed in Table III. Data from National Bureau of Standards Circular 500 for water and carbon dioxide were used for the latter.[12]

(12) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

5. Spectra. The spectra in Figure 2 were taken in ethanol solution with a Cary Model 15 (Applied Physics Corp.) recording spectrophotometer.

Discussion

In this section thermochemical stabilization energies are derived. These can be obtained from comparison of the experimental heat of combustion (or formation) with that expected for an appropriate reference structure. The latter can be calculated conveniently from a group contribution scheme.[13] Another equivalent but more direct way to obtain stabilization energies is to compare experimental enthalpies of two similar reactions, one for the compound of interest and one expected to be appropriate for the reference structure. We have used both approaches in this work and Table IV lists stabilization energies arrived at by both methods.

1. Acenaphthene. Of interest here is the strain in the bridging ring. Table IV lists values from the group contribution method[13] and from the comparison of reactions A and B listed under acenaphthene. It is seen that the strain energy is ∼6–7 kcal. mole^{-1}. This is comparable to the strain in other five-membered rings, *i.e.*, 6 kcal. mole^{-1} for cyclopentane and 4 kcal. mole^{-1} for cyclopentene.[14] Since an accurate X-ray structure is available,[10,15] it is of interest to calculate

(13) See, for example, Table IV, footnote *b*.
(14) Calculated from comparison of data in F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, and the group contribution scheme of ref. 13.
(15) The C—C—C angle strains reported are (structure III): $\angle C_1$–C_r–

Table III. Summary of Thermochemical Data at 25°

Compd.		$\Delta H_c°$, kcal. mole^{-1}	ΔH_{vap},[a] kcal. mole^{-1}	$\Delta H_f°$, kcal. mole^{-1}
Acenaphthylene	(c)	-1446.5 ± 1.1[b]	17.0 ± 0.3	44.7 ± 1.1
	(g)	-1463.5 ± 1.4[c]		61.7 ± 1.4
Acenaphthene	(c)	-1487.0 ± 0.6[b]	20.6 ± 0.3[d]	16.8 ± 0.6
	(g)	-1507.6 ± 0.9[c]		37.4 ± 0.9
Fluoranthene	(c)	-1892.4 ± 1.3[b]	24.4 ± 0.5[d]	46.0 ± 1.3
	(g)	-1916.8 ± 1.8[c]	$(55-80°)$	70.4 ± 1.8

[a] Uncertainty is arbitrary estimate. [b] Uncertainty is $\pm\sigma\Delta H_c°$, where $\sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$ and σ_1 and σ_2 are relative standard deviations of calibration and sample runs. [c] Uncertainty is summed uncertainty of a and b. [d] To be compared with literature values: acenaphthene, 19.9 kcal. mole^{-1}, and fluoranthene, 23.9 kcal. mole^{-1}: H. Hoyer and W. Peperle, *Z. Elektrochem.*, **62**, 61 (1958).

the strain from bond deformation force constants and the known deformations. However accurate force constants for complex molecules are very scarce. Using a value[16-18] of 0.8×10^{-11} erg/rad^2 for *all* of the C—C—C angle deformations (and neglecting C—C—H angle strain) leads to a value of the angle strain energy of 6.5 kcal. mole^{-1} which is very close to the observed strain. Inclusion of eclipsed hydrogen strain in the bridging group would increase the strain energy $\sim$1–2 kcal. mole^{-1}.

2. Acenaphthylene. The double bond of the bridging ring appears to have a definite interaction through conjugation with the naphthalene system as judged by the stabilization energy. The ring strain is nearly offset by this stabilizing interaction and the net strain is lowered to $\sim$2 kcal. mole^{-1}. The second set of reactions (A', B') for acenaphthylene also shows this stabilizing influence. Prompted by the similarity in strain energy of cyclopentane and cyclopentene, we might utilize acenaphthene as a reference for the ring strain, in which case the double bond in acenaphthylene is stabilized to the extent of -4 kcal. mole^{-1}.

3. Fluoranthene. The stabilizing influence of the bridging benzene ring appears to be less than the double bond as the net effect is a strain of 6–7 kcal. mole^{-1}, similar to that of the saturated acenaphthene.

4. Spectra. The qualitative conclusions from the ultraviolet spectra do not correlate particularly well with the thermochemical findings. However this is not surprising since the spectra involve strain and conjugation effects in both the ground *and* excited states. Acenaphthene (Figure 2) shows both an increase in intensity and shift to longer wave length compared to naphthalene. Such changes with strain and substitution are not unknown.[19,20] Since this would also be

the expected effect of conjugation, it is apparent that the spectra will not differentiate clearly between strain and conjugation. Acenaphthylene shows a further shift to longer wave length and increase in intensity that would correlate with the conjugation stabilization found thermochemically. However, fluoranthene absorbs at still longer wave lengths which would not be expected on the basis of the thermochemical evidence of smaller conjugation stabilization.
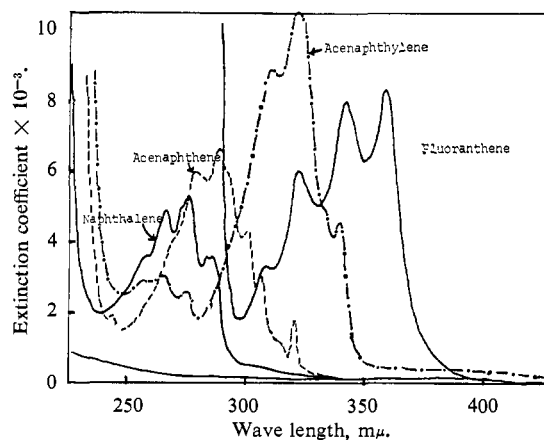

Figure 2. Ultraviolet absorption spectra of compounds studied compared with naphthalene.

Appendix

The Correction to Standard States. For the combustion of hydrocarbons under the usual conditions and to the accuracy of a few parts per 10,000, the only two appreciable terms in the correction to standard states from the actual bomb process (assuming the initial temperature is the same as the reference temperature) are the difference in compression energies of the gases in the initial and final states and the energy of solution of carbon dioxide in the bomb liquid in the final state. For the former, the usual method[8] is to calculate the compression energies for the initial and final states separately. However the relative pressure and composition changes of the gas are fairly small and the difference in compression energy can be directly calcu-

C_3, 12° (from 120°); $\angle C_2$–C_1–C_2', 8° (from 120°); $\angle C_2$–C_3–C_3', 4° (from 109° 28'). The bond lengths are normal.

(16) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.
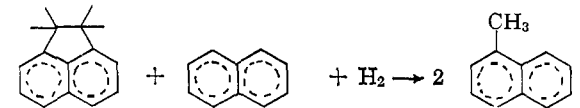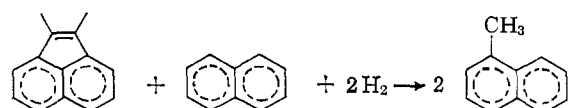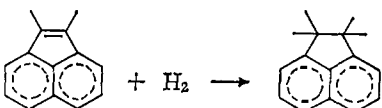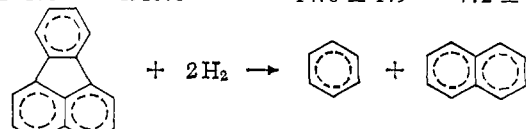
(17) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).

(18) A value of $k\gamma$ ($\gamma = \angle C$—C—C) $= 1.6 \times 10^{-11}$ erg/rad^2 ($= 1.1 \times 10^6$ cm.$^{-2} \times (0.05937)(1.54 \times 10^{-8})^2$) has been used for calculations on cyclopentane and also for $\gamma = \angle C$—C=C in cyclopentene. See R. S. Levedev and A. V. Sechkarev, *Opt. Spectry.* (USSR) (English Transl.), **7**, 104 (1959); L. M. Sverdlov and E. N. Krainov, *ibid.*, **6**, 214 (1959); G. I. Rybakova, D. S. Koval'chek, and V. P. Morozov, *ibid.*, **9**, 18(1960).

(19) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 11.

(20) The spectrum of acenaphthene is very similar to that of 1,8-dimethylnaphthalene: H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 307.

Table IV. Thermochemical Stabilization Energies,[a] ΔH_S

(References to thermochemical data used)	(1) $-\Delta H_C{}^\circ$ (exp.)	(2) $-\Delta H_C{}^\circ$ (reference structure)[b]	(3) $\Delta H_A{}^\circ$	(4) $\Delta H_B{}^\circ$	(5) ΔH_S (group contribution) (1) − (2)	(6) ΔH_S (direct) (4) − (3)
Acenaphthene	1507.6 ± 0.9	1502.0	−17.8 ± 1.6	−10.0	5.6 ± 0.9	7.8 ± 1.6
c, d						
e	B. R_1—CH$_2$—CH$_2$—R$_2$ + H$_2$ → R_1—CH$_3$ + R$_2$—CH$_3$					
Acenaphthylene	1463.5 ± 1.4	1462.5	−42.1 ± 1.6	−39.0	1.0 ± 1.4	3.1 ± 1.6
c, e						
e	B. R_1—CH$_2$—CH$_2$—R$_2$ + 2H$_2$ → R_1—CH$_3$ + R$_2$—CH$_3$		−24.3 ± 1.7	−28.5		−4.2 ± 1.7
e	B'. R_1—CH=CH—R$_2$ + H$_2$ → R_1—CH$_2$—CH$_2$—R$_2$					
Fluoranthene	1916.8 ± 1.8	1910.8	−14.6 ± 1.9	7.2 ± 1.5	6.0 ± 1.8	7.2 ± 2.4
c, e						
e, f						

A. (acenaphthene structure) + (naphthalene structure) + H$_2$ → 2 (1-methylnaphthalene structure)

A. (acenaphthylene structure) + (naphthalene structure) + 2 H$_2$ → 2 (1-methylnaphthalene structure)

A'. (structure) + H$_2$ → (structure)

A. (fluoranthene structure) + 2 H$_2$ → (benzene structure) + (naphthalene structure)

B. 2 (biphenyl structure) + 2 H$_2$ → 4 (benzene structure)

[a] All units are in kcal. mole^{-1}. The stabilization energy is taken as ΔH for A(reference) → A(actual), or $\Delta H_f{}^\circ$(actual) − $\Delta H_f{}^\circ$(reference) = ΔH_S; a negative stabilization energy indicates an actual structure more stable than the reference, in analogy with binding energies, etc. [b] Taken from Wheland's adaptation of Franklin's group contribution scheme: G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Chapter 3. The resonance energies of the naphthalene and benzene nuclei have been subtracted where appropriate from $-\Delta H_C{}^\circ$ in order to include them in the reference structure. [c] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960). [d] Reactions of the type A shown above were used instead of

(structure) + H$_2$ → (structure)
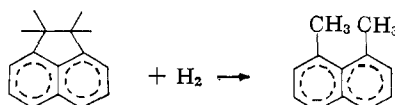
because of the availability of accurate data for 1-methylnaphthalene and also because this avoids the possibility of strain between methyl groups in the 1,8-compound. [e] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [f] G. S. Parks and L. M. Vaughan, *J. Am. Chem. Soc.*, **73**, 2380 (1951); R. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, 1690 (1953).

lated by a perturbation technique with sufficient accuracy and appreciable savings in computational labor. Following ref. 8, let the derivative of energy mole^{-1} with respect to pressure for O$_2$ and O$_2$-CO$_2$ mixtures be

$$\left(\frac{\partial E}{\partial P}\right)_{T(O_2)} = A \tag{A-1}$$

and

$$\left(\frac{\partial E}{\partial P}\right)_{T(O_2+CO_2)} = A[1 + \beta] \tag{A-2}$$

where β is a function of CO$_2$ content. The total gas compression correction, q_c, is then

$$q_c = AP_i n_i - A(1 + \beta)P_f n_f \tag{A-3}$$

where i and f refer to initial and final states, P is pressure, and n is the total number of moles of gas (O$_2$ and O$_2$ + CO$_2$). Let $n_f = n_i + \Delta n$ and $P_f = P_i +$

ΔP; then to first-order quantities

$$q_c = -A[\beta P_i n_i + (1 + \beta)(n_i \Delta P + \Delta n P_i)] \tag{A-4}$$

where $A = -1.574$ cal. atm.$^{-1}$ mole.$^{-1}$ at 25° and $\beta = 1.69 X(1 + X)$, where X is the mole fraction of gaseous CO$_2$ in the final state.[8] n_i is a constant of the bomb for a given initial pressure (calculated from eq. A-5) and Δn is easily calculated from the bomb reaction. ΔP is calculated as follows. Following ref. 8

$$P_i = n_i \frac{RT}{V}(1 - \mu_{O_2} P_i) \tag{A-5}$$

and

$$P_f = n_f \frac{RT}{V}(1 - \mu_f P_f) \tag{A-6}$$

with $\mu_f = \mu_{O_2}(1 + \alpha)$.

To first order

$$\Delta P = -\alpha\mu_{O_2}P_i{}^2 + \Delta n \frac{RT}{V} \qquad \text{(A-7)}$$

where $\mu_{O_2} = 6.07 \times 10^{-4}$ atm.$^{-1}$ at 25° and

$$\alpha = 3.21X(1 + 1.33X)$$

where X is the mole fraction of CO_2 in the final state.[8] RT/V is a constant of the bomb.

The corrections to standard states in this paper were made using eq. A-4 and A-7. The energy of solution of CO_2 in the bomb liquid is negligible for our work for the liquid volumes present. The initial temperatures for the combustions were at 25.00°, the same as the reference temperature.

Iodine Complexes with Cyclohexanone and Related Compounds[1]

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Studies were made of the ultraviolet and visible absorption spectra of iodine complexes with cyclohexanone and related compounds in Freon solution. Charge-transfer bands occur at 242 mμ for acetone, 249 mμ for 2-cyclohexenone, 233 mμ for cyclohexanol, and 253 mμ for both cyclopentanone and cyclohexanone complexes. Equilibrium constants, extinction coefficients, and enthalpies for these complexes are given. At higher concentrations of the ketones, a second type of complex with absorption maxima at 300 and 375 mμ dominates the spectra. Since its concentration varies as the square of the first complex concentration, it is thought to be a dimer complex. The dimer complexes have unusually high formation energies of about 20 kcal./mole.

I. Introduction

It is now generally believed that the noninert solvents for iodine which result in a color other than violet form charge-transfer complexes with iodine.[3] More particularly, it has been suggested that oxygen-containing solvents form iodine complexes through the oxygen lone-pair electrons. Although ketones appear to form strong complexes, they have not been studied extensively, possibly because iodination is thought to occur easily.[4] Iodination can usually be avoided or delayed by dilution in an inert solvent, by cooling, and by minimum exposure to light. Infrared studies of acetone and cyclohexanone in solution with iodine have demonstrated that a complex is formed and that the iodine molecule is bound to the keto oxygen.[5]

II. Experimental

Measurements of the visible and ultraviolet absorption spectra were made with a Perkin-Elmer Type 202 spectrophotometer using 1- and 10-mm. absorption cells. Temperature was held to within ±0.2° of a preset value in the range −15 to +35° by means of an automatic temperature control.

Reagent grade acetone, cyclohexanone, cyclohexanol, and cyclopentanone were used without further purification except drying with Drierite. Hexachloroacetone (m.p. −5°) was recrystallized from dichlorodifluoromethane; 2-cyclohexenone was purified by fractional distillation (b.p. 42° at 5 torr). Trichlorotrifluoroethane, a Freon (F-113) which boils at 47°, was selected because it is an inert solvent[6] of fairly high solubilization, is readily available in pure form (Dupont), and is transparent sufficiently far in the ultraviolet (230 mμ).

III. Monomer Complex Formation

When acetone, cyclopentanone, cyclohexanone, or 2-cyclohexenone, and iodine are dissolved in an inert solvent, two absorption bands appear in addition to those present in iodine and ketone (Z) alone, as shown in Figures 1 and 2. These two bands are attributed to a 1:1 charge-transfer complex (X_1). The visible peak of

$$Z + I_2 \rightleftharpoons X_1$$
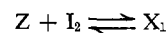
the complex at 465 mμ lies close to the normal visible I_2 band at 520 mμ (ϵ 870) and is due to a shift of the normal I_2 band.[3] The ultraviolet peak at 230–260 mμ is identified as the charge-transfer band.

Because of the limited solubility of iodine in Freon ($\sim 10^{-2}$ M), an excess of ketone was used to produce a measurable concentration of the complex. Only a small fraction of the ketone was found as a complex so that its concentration at all times was practically equal to the initial concentration. Thus, its ultraviolet absorption spectrum could be subtracted from the total spectrum.

Often an appreciable fraction of the iodine was bound in the complex. The free iodine can be measured spectrophotometrically if allowance is made for absorption of the complex which overlaps the free iodine band. A spectral subtraction procedure indicated a

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(2) Fellow of the USPHS Training Program at Roswell Park Memorial Institute.

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