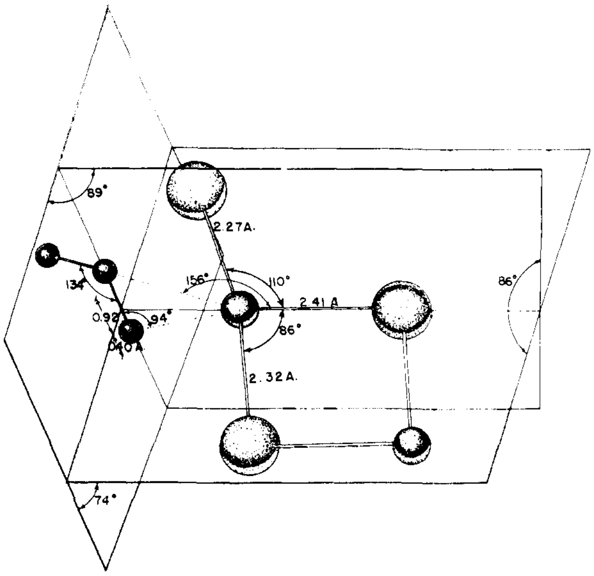

Fig. 3.—Detail sketch of the styrene–palladium chloride complex. The large atoms are chlorine, the medium size atoms are palladium, and the smallest are the carbon atoms, C_1, C_7 and C_8 of styrene. The intersection of the three planes lies at 0.40 Å. from carbon atom C_8.

The configuration of the atoms in styrene–palladium chloride is, therefore, entirely consistent with the theory that the palladium–olefin bond consists of interaction between one of the dsp^2 hybrid orbitals of palladium and the pi orbital of the double bond. The palladium orbital enters the pi bond off center and forms an angle of 74 degrees with the double bond axis. The structure of ethylene–palladium chloride indicates, however, that the palladium orbital enters the ethylene pi bond at its center and forms an angle of 90 degrees with the double bond axis. The ethylene molecule is symmetrical about its double bond; whereas, in styrene, where one of the carbons of the double bond is attached to the large phenyl group, the bond from palladium is off center. There are several possible causes for the displacement of the palladium bond toward the end carbon of the styrene molecule. (1) There may be an asymmetrical distribution of electrons in the pi bond of the ethylene side-chain, the carbon atom C_8 being more negative. (2) Rotation of the ethylene group into a position such that the carbon atoms are equidistant from the palladium atom requires, either that the ethylene side chain be twisted far out of the plane of the benzene ring, or that the molecules assume an entirely new packing arrangement in the solid. Either alternative could increase the crystal energy.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

The Thermodynamic Functions of Bis-cyclopentadienyl Iron, Bis-cyclopentadienylnickel and Bis-cyclopentadienylruthenium

BY ELLIS R. LIPPINCOTT* AND RICHARD D. NELSON

RECEIVED APRIL 29, 1955

The thermodynamic quantities C_p^0, $(H^0 - E_0^0)/T$, $-(F^0 - E_0^0)/T$ and S^0 have been calculated from 298.16 to 1500°K. for bis-cyclopentadienyliron(II), nickel(II) and ruthenium(II) from an assignment of frequencies based on infrared and Raman spectroscopic studies. The quantities ΔH_f^0, ΔF_f^0 and ΔS_f^0 have been calculated for $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$ from 298.16 to 1500°K. Thermodynamically $Ru(C_5H_5)_2$ is the most stable and $Ni(C_5H_5)_2$ the least stable of these three compounds.

Introduction

The unusual sandwich structures of a number of the transition metal dicyclopentadienyl compounds have stimulated a wide range of studies concerning their chemical and physical properties.[1-8] The structures of these compounds have been demonstrated conclusively and the aromatic nature of the cyclopentadienyl rings established.[9-13] However the nature of the forces binding the rings to the metal atom is only partially understood and there is no complete agreement as to how best to describe the type of bonding involved. A tabulation of the calculated thermodynamic functions for some representative examples of this interesting series of compounds is then desirable for a comparison with their other properties. We are carrying out a detailed spectroscopic study of a number of metal cyclopentadienyl compounds. The results of the vibrational analysis on $Fe(C_5H_5)_2$, $Ru(C_5H_5)_2$ and $Ni(C_5H_5)_2$ are nearly complete and permit a reliable assignment of frequencies to be made to the fundamental modes of vibration for these molecules. We wish to present here tabulations of a number of thermodynamics functions at 100° intervals from 300 to 1500°K. for these three molecules based on this assignment. At this time no heat capacity or entropy measurements are available for comparison. When such thermal measurements are available a comparison of the experimental and calculated thermodynamic quantities will furnish information concerning the possible existence of a barrier preventing free internal rotation of the cyclopentadi-

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enyl rings and permit an estimate of its magnitude.

Thermodynamic Functions.—The heat capacity, enthalpy, free energy and entropy functions were calculated by standard methods using the vapor phase rigid rotator, harmonic oscillator approximation. The structural data for $Fe(C_5H_5)_2$ were taken from the results of Eiland and Pepinsky.[10] Their results give a C–C distance of 1.41 Å. and Fe–C distance of 2.0 Å. By analogy with benzene the C–H distance was assumed to be 1.08 Å. Using these data with a molecular symmetry of D_{5d} the principal moments of inertia I_A and I_B are calculated as 355.6×10^{-40} and 731.7×10^{-40} g. cm.^{2}, respectively. The structural information for $Ru(C_5H_5)_2$ and $Ni(C_5H_5)_2$ is nearly the same as for $Fe(C_5H_5)_2$. A symmetry number of 10 was used corresponding to D_{5d} symmetry.

The vibrational contribution to the thermodynamic functions of these compounds was made using the three assignments given in Table I. The assignment for $Fe(C_5H_5)_2$ is based on a spectroscopic study of both $Fe(C_5H_5)_2$ and its deuterium derivative $Fe(C_5D_5)_2$. Infrared spectra in the region from 300 to 4000 cm.$^{-1}$ were obtained on the vapor and solid phases as well as in solution. Raman spectra of $Fe(C_5H_5)_2$ and $Fe(C_5D_5)_2$ were obtained in solution from 100 to 3500 cm.$^{-1}$. This assignment was supported by a normal coördinate analysis for a number of the inactive frequencies. The assignment for $Ru(C_5H_5)_2$ was based on a similar spectroscopic study and normal coördinate analysis with the exception that data on $Ru(C_5D_5)_2$ were not available. The assignment for $Ni(C_5H_5)_2$ is somewhat more empirical than that for $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$ in that no Raman spectrum was obtained with the result that more emphasis was placed on frequency positions and normal coordinate calculations similar to those for $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$. However the errors due to incorrect assignment are believed to be small enough to permit a reasonably reliable calculation of thermodynamic functions.

For all three molecules the inactive A_{1u} ν_6 frequency was assumed to correspond to a free internal rotation. The contribution to the entropy for this internal rotation was calculated from the equation[14]

$$S^0_{\text{f.i.r.}} = (\ln T + \ln (I_A/4) - 2 \ln 5 + \ln (8\pi^3 k/h^2) + 1)\, R/2$$

The calculated thermodynamics functions C^0_p, $(H^0 - E^0_0)/T$, $-(F^0 - E^0_0)/T$ and S^0 are tabulated in Table II. A breakdown of the total S^0 and C^0_p into rotational, translational, vibrational and free internal rotational contributions at 298.16°K. is given in Table III.

Thermodynamic Functions of Formation for $Fe(C_5H_5)_2(g)$ and $Ni(C_5H_5)_2(g)$.—The calculated values of ΔH^0_f, ΔF^0_f and ΔS^0_f for the formation of $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$ from their elements in their standard states at various temperatures are tabulated in Table IV. The heats of formation of $Fe(C_5H_5)_2(s)$ and $Ni(C_5H_5)_2(s)$ have been given by Wilkinson[14,15] as 33.8 and 62.8 kcal. per mole, respectively. The heat of sublimation for $Fe(C_5H_5)_2$ has been given by Kaplon, Kester and Katz[16] as 16.81 kcal. per mole. Following Wilkinson we have assumed the heat of sublimation of $Ni(C_5H_5)_2$ to be the same as that for $Fe(C_5H_5)_2$ because of the close similarity of their physical properties.[8] The thermodynamic functions of iron and nickel at various temperatures were taken from the data of Kelley.[17,18] Because their data is given at irregular temperature intervals it was found necessary to replot their data to obtain data for our temperatures. These data along with the heats of formation, free energies of formation and entropies of graphite and hydrogen in their standard states[19] were combined

TABLE I

ASSIGNMENT OF FREQUENCIES[a] FOR $Fe(C_5H_5)_2Ni(C_5H_5)_2$ AND $Ru(C_5H_5)_2$, CM.$^{-1}$

Species[b]		Description[c,d]	Fe-$(C_5H_5)_2$	Ni-$(C_5H_5)_2$	Ru-$(C_5H_5)_2$
A_{1g}	1	CH stretch	3099	3100	3104
	2	CH bend (⊥)	804	770	805
	3	*sym*-ring breathing	1105	1105	1104
	4	*sym*-ring metal stretch	303	220	330
A_{1u}	5	CH bend (‖)	1200	1200	1200
	6	Internal rotation	..	..	..
A_{2g}	7	CH bend (‖)	1200	1200	1200
A_{2u}	8	CH stretch	3085	3075	3100
	9	CH bend (⊥)	811	773	806
	10	*anti–sym*-ring breathing	1108	1110	1103
	11	*anti–sym*-ring metal stretch	478	355	456
E_{1g}	12	CH stretch	3085	3085	3089
	13	CH bend (‖)	1010	1010	996
	14	CH bend (⊥)	800	770	804
	15	*sym*-CC stretch	1408	1430	1412
	16	*sym*-ring tilt	388	275	402
E_{1u}	17	CH stretch	3075	3075	3100
	18	CH bend (‖)	1002	1000	1002
	19	CH bend (⊥)	834	800	800
	20	*anti–sym*-CC stretch	1411	1428	1413
	21	*anti–sym*-ring tilt	492	355	528
	22	Ring metal ring bend	150	110	165
E_{2g}	23	CH stretch	3085	3085	3089
	24	CH bend (‖)	1178	1180	1193
	25	CH bend (⊥)	1050	1050	1056
	26	CC stretch	1590	1590	1590
	27	Ring distortion (‖)	900	900	900
	28	Ring distortion (⊥)	500	500	500
E_{2u}	29	CH stretch	3100	3100	3100
	30	CH bend (‖)	1170	1170	1170
	31	CH bend (⊥)	1050	1050	1050
	32	CC stretch	1550	1550	1550
	33	Ring deformation (‖)	900	900	900
	34	Ring deformation (⊥)	500	500	500

[a] The basis for this assignment will be given in a forthcoming publication. [b] Raman active species A_{1g}, E_{1g}, E_{2g}; Infrared active species A_{2u} and E_{1u}; inactive species A_{1u}, A_{2g} and E_{2u}. [c] (‖) and (⊥) indicate displacements which are parallel and perpendicular to the planes of cyclopentadienyl rings, respectively. [d] The frequencies in species E_{1g}, E_{1u}, E_{2g} and E_{2u} are doubly degenerate and must be assigned a weight of two in the thermodynamic calculations.

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TABLE II

THERMODYNAMIC FUNCTIONS FOR $Fe(C_5H_5)_2(g)$, $Ru(C_5H_5)_2$-(g) AND $Ni(C_5H_5)_2(g)$

T, °K.	C_p^0	$(H^0 - F_0^0)/T$	$-(F^0 - F)/T$	S^0
		$Fe(C_5H_5)_2$		
298.16	38.05	19.82	68.17	87.99
300	38.29	19.93	68.29	88.22
400	51.67	26.23	74.89	101.12
500	62.61	32.45	81.39	113.84
600	71.18	38.24	87.85	126.09
700	77.96	43.44	94.15	137.59
800	83.45	48.10	100.25	148.35
900	88.00	52.29	106.17	158.46
1000	91.84	56.08	111.89	167.97
1100	95.07	59.47	117.39	176.86
1200	97.82	62.54	122.69	185.23
1300	100.20	65.35	127.80	193.15
1400	102.25	67.92	132.75	200.67
1500	104.01	70.26	137.48	207.74
		$Ru(C_5H_5)_2$		
298.16	37.94	19.56	68.42	87.98
300	38.18	19.66	68.54	88.20
400	51.66	26.03	75.08	101.11
500	62.62	32.28	81.53	113.81
600	71.19	38.08	88.00	126.08
700	77.96	43.33	94.19	137.52
800	83.44	47.97	100.29	148.26
900	87.98	52.19	106.24	158.43
1000	91.81	56.01	111.98	167.99
1100	95.07	59.39	117.44	176.83
1200	97.80	62.47	122.74	185.21
1300	100.19	65.29	127.79	193.09
1400	102.22	67.86	132.78	200.65
1500	103.98	70.20	137.53	207.73
		$Ni(C_5H_5)_2$		
298.16	39.93	21.80	70.61	92.41
300	40.17	21.92	70.74	92.66
400	53.01	28.13	77.91	106.04
500	63.58	34.18	84.81	118.99
600	71.89	39.81	91.60	131.41
700	78.51	44.89	98.11	143.01
800	83.86	49.43	104.41	153.84
900	88.32	53.52	110.46	163.98
1000	92.09	57.22	116.34	173.56
1100	95.29	60.52	121.92	182.44
1200	97.99	63.52	127.31	190.83
1300	100.35	66.27	132.50	198.77
1400	102.36	68.78	137.42	206.20
1500	104.11	71.05	142.30	213.35

TABLE III

Cp^0 AND S^0 FOR $Fe(C_5H_5)_2$, $Ru(C_5H_5)_2$ AND $Ni(C_5H_5)_2$

	Rotational	Translational	Vibrational	Free internal rotational	Total (cal./mole degrees)
			$Fe(C_5H_5)_2$		
S^0	24.44	41.55	16.62	5.38	87.99
Cp^0	2.98	4.95	29.13	0.99	38.05
			$Ru(C_5H_5)_2$		
S^0	24.44	42.21	15.95	5.38	87.98
Cp^0	2.98	4.95	29.02	0.99	37.94
			$Ni(C_5H_5)_2$		
S^0	24.44	41.60	20.99	5.38	92.41
Cp^0	2.98	4.95	31.00	0.99	39.92

TABLE IV

THERMODYNAMIC FUNCTIONS OF FORMATION FOR $Fe(C_5H_5)_2$-(g) AND $NI(C_5H_5)_2(g)$

T, °K.	$(\Delta H)_f^0$, kcal./mole	$(\Delta F)_f^0$, kcal./mole	$(\Delta S)_f^0$, cal./mole
	$Fe(C_5H_5)_2$		
298.16	50.61	75.97	−85.07
300	50.55	76.16	−85.37
400	48.49	85.29	−92.01
500	46.91	94.93	−96.05
600	45.61	104.83	−98.71
700	44.45	114.96	−100.74
800	43.53	125.24	−102.13
900	42.71	135.60	−103.21
1000	41.86	146.07	−104.21
1100	41.18	156.63	−104.95
1200	40.48	167.25	−105.63
1300	40.33	177.90	−105.82
1400	40.21	188.53	−105.95
1500	40.12	199.26	−106.09
	$Ni(C_5H_5)_2$		
298.16	79.61	103.80	−81.10
300	79.58	104.02	−81.45
400	77.68	112.72	−87.59
500	76.12	121.92	−91.61
600	74.91	130.76	−93.10
700	73.80	141.02	−96.03
800	73.04	150.84	−97.25
900	72.44	160.73	−98.10
1000	72.06	170.63	−98.57
1100	71.78	180.64	−98.96
1200	71.61	190.64	−99.19
1300	71.50	200.64	−99.34
1400	71.42	210.77	−99.54
1500	71.34	220.72	−99.59

with the data in Table II to obtain the calculated values of ΔH_f^0, ΔF_f^0 and ΔS_f^0 for the reactions of formation

$$10C(s) + 5H_2(g) + Fe(s) \longrightarrow Fe(C_5H_5)_2(g)$$
$$10C(s) + 5H_2(g) + Ni(s) \longrightarrow Ni(C_5H_5)_2(g)$$

These functions are reported at various temperatures in Table IV. The values given for the standard heats of formation at 0°K., ΔH_{f0}^0, for $Fe(C_5H_5)_2(g)$ and $Ni(C_5H_5)_2(g)$ are 57.5 and 79.6 kcal./mole, respectively.

Discussion

The thermodynamic functions C_p^0 and S^0 calculated for these compounds are all considerably lower than most metalorganic compounds of comparable molecular weight, the effect being particularly evident with $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$. This result is expected in view of the stability and high symmetry of these compounds.

The calculated functions C_p^0, $(H^0 - E_0^0)/T$, $-(F^0 - E_0^0)/T$ and S^0 for $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$ are nearly the same. This accidental result arises because of two opposing effects. If the cyclopentadienyl rings of $Ru(C_5H_5)_2$ were bound to the metal atom with the same energy as in $Fe(C_5H_5)_2$, the calculated thermodynamic functions for $Ru(C_5H_5)_2$, would be larger than those for $Fe(C_5H_5)_2$ because of the higher molecular weight of $Ru(C_5H_5)_2$. That the rings are bound with greater energy in $Ru(C_5H_5)_2$ is seen by comparing the ring–metal–ring symmetric stretching frequencies of $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$ which appear at 303 and 330 cm.$^{-1}$, respectively. Corresponding increases in several other frequencies occur with the result that the increase in molecular weight of $Ru(C_5H_5)_2$ is compensated completely by the higher set of frequencies resulting from increased stability. Actually the calculated S^0 for $Ru(C_5H_5)_2$ is slightly less than that for $Fe(C_5H_5)_2$.

A comparison of the thermodynamic functions of $Ni(C_5H_5)_2$ with $Fe(C_5H_5)_2$ are significantly different. Since these compounds have nearly the same molecular weight, this difference is due to the much greater stability of $Fe(C_5H_5)_2$.

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MANHATTAN, KANSAS

[CONTRIBUTION NO. 49 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

2,3-Dimethyl-2-butene: Thermodynamic Properties in the Solid, Liquid and Vapor States

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Various thermodynamic properties of 2,3-dimethyl-2-butene were studied experimentally. The entropy of the liquid a 298.16°K. (S_{satd} = 64.58 cal. deg.$^{-1}$ mole^{-1}) was computed from calorimetric values of the heat capacity in the solid and liquid states (11 to 318°K.) and of the heats of transition and fusion (844 cal. mole^{-1} at 196.82°K. and 1542 cal. mole^{-1} at the triple point, 198.92°K., respectively). Results obtained for the heat capacity of the liquid (C_{satd}), vapor pressure (p), heat of vaporization (ΔH_v), heat capacity in the ideal gas state (C_p°), and the second virial coefficient [$B = (PV - RT)/P$] are represented as a function of temperature by the following empirical equations: (1) $C_{satd} = 48.178 - 0.16068T + 6.2188 \times 10^{-4}T^2 - 5.2083 \times 10^{-7}\,T^3$, cal. deg.$^{-1}$ mole^{-1}) (200–320°K.); (2) $\log_{10}p$ (mm.) $= 6.93324 - 1206.037/(t + 224.400)$, (29–73°); (3) $\Delta H_v = 10{,}674 - 5.713T - 0.01344T^2$, cal. mole^{-1} (292–346°K.); (4) $C_p^\circ = 4.454 + 0.087361T - 1.1983 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (334–473°K.); and $B = -2764 - 4.93\ \exp.(1100/T)$, cc. mole^{-1} (292–473°K.). The entropy in the ideal gas state at 298.16°K. (S° = 87.16 cal. deg.$^{-1}$ mole^{-1}) was computed from these data. A vibrational assignment was made for 2,3-dimethyl-2-butene, and the average height of the potential barriers hindering internal rotation of the methyl groups, 680 cal. mole^{-1}, was evaluated from the calorimetric data. Values of the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° were calculated at selected temperatures to 1500°K.

As part of the continuing program of this Laboratory to measure thermodynamic properties of hydrocarbons important in petroleum technology, calorimetric studies were made on 2,3-dimethyl-2-butene. These included determination of the entropy of the vapor from Third Law studies and measurement of the heat capacity of the vapor. The methods of statistical mechanics were used to compute thermodynamic functions for the ideal gas state.

Experimental

The 1951 International Atomic Weights[1] and the 1951 values of the fundamental physical constants[2] were used for all computations described in this paper. Measurement of temperature above 90°K. was made in terms of the International Temperature Scale of 1948,[3] and International Celsius temperatures were converted to Kelvin temperatures by adding 273.16°. Below 90°K., the temperature scale was defined by a platinum resistance thermometer calibrated at the National Bureau of Standards in terms of the provisional scale established by Hoge and Brickwedde.[4] All electrical and mass measurements were referred to standards calibrated at the National Bureau of Standards. Energy measured in joules was converted to calories by use of the definitions 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

Material.—The 2,3-dimethyl-2-butene used for low temperature calorimetry and for measurement of vapor pressure was an A.P.I. Research sample.[5] In calorimetric melting point studies, this sample was found to contain 0.05 mole % liquid-soluble, solid-insoluble impurity. A second sample, of somewhat lower purity (about 99.5 mole %), supplied by A.P.I. Research Project 6, was used for the measurements of heat of vaporization and vapor heat capacity, which required a larger sample than the other studies. The samples of 2,3-dimethyl-2-butene were received in sealed ampoules with internal break-off tips and were stored in the dark at 5°. Transfers to appropriate receivers were made by vacuum distillation. At no time in the handling of the material or in the experiments were the samples in contact with gases other than helium. Such precautions were necessary to avoid oxidation of 2,3-dimethyl-2-butene by atmospheric oxygen. In the studies of heat of vaporization and vapor heat capacity, 0.02 mole % hydroquinone was added to the sample as inhibitor.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal properties of 2,3-dimethyl-2-butene were measured in an adiabatic cryostat similar to that described by Ruehrwein and Huffman.[6] The sample (about 0.44 mole) was sealed in a copper calorimeter that contained horizontal perforated disks to facilitate attainment of thermal equilibrium and prevent settling of the solid phase during fusion experiments. The observed values of heat capacity at saturation pressure (C_{satd}) of the solid and liquid are presented in Table I. The temperature increments used in the experiments were small enough that corrections for non-linear variation of C_{satd} with T were unnecessary (the

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