[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY AND DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Thermodynamic Functions of Cycloöctatetraene[1]

BY E. R. LIPPINCOTT[2] AND R. C. LORD

The thermodynamic quantities C_p^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, S^0, ΔH_f^0, ΔS_f^0 and ΔF_f^0 have been calculated for cycloöctatetraene over the temperature range 298.16–1000°K. from spectroscopic and electron-diffraction data. The calculated value of S^0_{298} is 77.76 e.u. to be compared with a measured value of 78.10 ± 0.35. It is concluded that the close similarity in the reasonable vibrational assignments of the crown (D_4) and tub (D_{2d}) structures precludes distinguishing at the present time between the two structures by methods of statistical mechanics such as the comparison of calculated and measured entropy values. The equilibrium constants for the formation of cycloöctatetraene by polymerization of acetylene, by isomerization of styrene and by reaction of benzene and acetylene are tabulated for various temperatures up to 1000°K.

The completion of an analysis of the vibrational spectra of cycloöctatetraene[3] enables the calculation of the thermodynamic functions for this molecule in the vapor phase. Such calculations are particularly valuable in view of recent careful measurements of the heats of combustion,[4] fusion and vaporization,[5] and of the low-temperature heat capacity[5] of cycloöctatetraene. It is now possible to calculate equilibrium constants for all the vapor phase reactions of cycloöctatetraene that involve molecules whose thermodynamic functions are likewise known. It is also possible to check the vibrational assignment to a certain extent by the agreement between the calorimetric and the spectroscopic entropy, and by the success with which a semi-empirical calculation[6] of the heat capacity curve of the crystal duplicates the observed curve.

The vapor-phase thermodynamic functions were calculated by the standard methods.[7] For this purpose, the gas constant R was taken as 1.9863 calories/mole/degree, N as 6.024×10^{23} molecules/mole, and the atomic weights of hydrogen and carbon as 1.008 and 12.01. The moments of inertia were calculated on the basis of a crown structure (D_4 symmetry) from the dimensions of Hedberg and Schomaker,[8] whose electron-diffraction studies, however, led them to conclude that the molecule was of the tub form (D_{2d} symmetry).[9] The assumed distances and angles were: carbon–carbon double bond, 1.34 Å.; carbon–carbon single bond, 1.45 Å.; carbon–hydrogen bond, 1.08 Å.; C–C–C bond angle, 127°. Each carbon–hydrogen bond was assumed to lie in the plane of the two adjoining carbon–carbon bonds, and to bisect their angle of intersection. From these assumptions and the geometry of the D_4 structure, the moments of inertia are calculated to be: $I_{x,y} = 303 \times 10^{-40}$ g.-sq. cm.; $I_z = 580 \times 10^{-40}$ g.-sq. cm.

To complete the calculation of the rotational contribution to the thermodynamic functions, a knowledge of the symmetry number σ is needed. A D_4 structure has a symmetry number of 8, but this number can only be used with due regard for the fact that D_4 symmetry implies optical isomerism. The two optical isomers have the same moments of inertia, the same vibration frequencies and the same symmetry number, but when the vapor-phase entropy of a 50–50 mixture of the isomers is calculated, the entropy of mixing ($+R \ln 2$) must be included. Inasmuch as the symmetry number enters the entropy through the term $-R \ln \sigma$, the entropy of mixing has the apparent effect of cutting the symmetry number in half, *i.e.*, from 8 to 4.

In order to draw conclusions from a comparison of the spectroscopic entropy with the calorimetric, one must first consider the question of the persistence of the entropy of mixing in the crystal. If the dextro and levo forms do not interconvert readily and if they can enter the crystal randomly, the entropy of mixing can perist in the crystal down to the absolute zero. In this event the entropy of mixing would not appear in the calorimetric entropy and the spectroscopic entropy would agree with the calorimetric only if the mixing term were omitted. On the other hand, if the dextro and levo forms were freely interconvertible even in the crystal, it would be expected that entropy of mixing could be removed by cooling the crystal, and that the calorimetric entropy would then contain the entropy of mixing. In the intermediate case of some residual entropy of mixing at absolute zero, the residuum could be determined by comparison of the spectroscopic and calorimetric entropies. This determination, of course, would be reliable only if there were no other difficulties (such as erroneous vibrational assignments) with the former and no question of large experimental error in the latter.

No evidence has yet been produced of optical activity in cycloöctatetraene. In an attempt to fractionate the supposed isomers, Howard and Lord[10] passed the compound dissolved in petroleum ether through a chromatographic column filled with optically active quartz powder. No optical activity resulted, although the same procedure was successful in producing optical activity in an inactive synthetic mixture of pure *d*- and *l*-carvone. Apart from the obvious explanation that cycloöctatetra-

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(2) Department of Chemistry, University of Connecticut, Storrs, Connecticut.

(3) Lippincott, Lord and McDonald, THIS JOURNAL, **73**, 3370 (1951).

(4) Prosen, Johnson and Rossini, *ibid.*, **69**, 2068 (1947); **72**, 626 (1950).

(5) Scott, Gross, Oliver and Huffman, *ibid.*, **71**, 1634 (1949).

(6) Lord, *J. Chem. Phys.*, **9**, 693 (1941).

(7) See, for example, Taylor and Glasstone, "Treatise on Physical Chemistry," Chap. IV; Herzberg, "Infrared and Raman Spectra," Chap. V.

(8) Hedberg and Schomaker, Abstracts, San Francisco meeting, American Chemical Society, March, 1949.

(9) Bastiansen and Hassel (*Acta Chem. Scand.*, **3**, 209 (1949)) from their electron-diffraction studies have reached essentially the same structural conclusion as ourselves. Their numerical data are in fair agreement with those of Hedberg and Schomaker, but the former investigators did not resolve the single-bond and double-bond distances. The data of Hedberg and Schomaker are therefore more complete for calculation of the moments of inertia.

(10) See R. O. Howard, Bachelor's Thesis, Department of Chemistry, Massachusetts Institute of Technology, June, 1949.

ene is not a mixture of optical isomers, this negative result could also have been obtained if the rate of interconversion of the optical isomers is rapid at room temperature.

The modes of vibration by means of which the interconversion can take place most directly are the three totally symmetrical ring vibrations. The modes give rise to polarized Raman lines at frequencies of 194, 873 and 1651 cm.$^{-1}$ in cycloöctatetraene and at 172, 822 and 1645 cm.$^{-1}$ in cyclooctatetraene-d_8. None of the lines shows a splitting that can be attributed to molecular inversion such as is exhibited by the ammonia molecule. In ammonia the first excited level of the totally symmetrical bending vibration is split by about 36 cm.$^{-1}$ out of 1000 cm.$^{-1}$. Here, however, the interconversion frequency in the ground state is extremely high (of the order of 10^{10} sec.$^{-1}$). The splitting of the totally symmetrical lines in cyclooctatetraene could be too small to observe (<1 cm.$^{-1}$) and the interconversion frequency could still be very rapid (several orders of magnitude faster than 1 sec.$^{-1}$).

The question of which of the ring vibrations is most effective in the interconversion can only be answered from a quantitative knowledge of the molecular potential function and the normal coördinates of each vibration. In the absence of such knowledge, it may be guessed to be the ring distortion vibration at 194 cm.$^{-1}$, which is most nearly analogous to the ammonia bending vibration. In an approximate treatment of inversion by means of this vibration to be published later by one of the present authors (R.C.L.), it was found that the interconversion frequency could be as high as 10^6 sec.$^{-1}$.[11]

If the interconversion rate is rapid at room temperature, we may reasonably expect it to be rapid in the crystal, at least near the melting point, because of the well-known fact that most internal vibrations in molecules change little on passing from the vapor to condensed phases. We may therefore also expect that at least some of the entropy of mixing of the optical isomers will be removed from the crystal as the temperature is lowered. On the assumption that all can be removed upon cooling to the neighborhood of 0°K., we shall include the entropy of mixing term in the spectroscopic entropy.

The Thermodynamic Properties of Cycloöctatetraene and their Relation to its Molecular Structure.—The thermodynamic properties of cyclooctatetraene calculated from the frequencies of ref. 3 and the other molecular data as described in the preceding text are listed in Table I. It is of interest to consider whether a comparison of these calculated values with experimentally determined quantities might yield some information about the structure. One possibility is a comparison of the theoretical and observed entropy values at 298°K., a procedure that has been used for other molecules, for example, benzene.[12] The calculated and observed values just barely agree within the estimated experimental error of the latter, $S^0_{298} = 78.10 \pm 0.35$ entropy units. If this agreement is significant, it means that there is little or no residual entropy in the crystal at 0°K., as would be expected on the basis of the discussion given above.

TABLE I

THERMODYNAMIC PROPERTIES OF CYCLOÖCTATETRAENE IN THE IDEAL GAS STATE IN CALORIES PER MOLE PER °K.

T	C_p^0	$\frac{(H^0 - H_0^0)}{T}$	$\frac{-(F^0 - H_0^0)}{T}$	S^0
298.16	29.16	16.42	61.34	77.76
400	38.45	20.90	66.78	87.67
500	46.38	25.25	71.98	97.23
600	52.77	29.34	76.92	106.27
700	57.90	33.01	81.65	114.66
800	62.23	36.47	86.31	122.78
900	65.75	39.49	90.78	130.27
1000	68.88	42.31	95.12	137.44

On the other hand, it is obvious from an inspection of the frequency assignment made on the basis of the D_{2d} structure[3] that reasonable estimates of the spectroscopically inactive frequencies in that structure would also give an entropy value close to the experimental one. It is therefore our conclusion that on the basis of present spectroscopic data as we have interpreted them, no decision between the D_4 and D_{2d} structures is possible from the entropy calculation.

We have also made a semi-empirical calculation[6] of the heat capacity of crystalline cycloöctatetraene. Such a calculation was useful in the benzene case[13] to distinguish between two rather drastically different assignments of the lowest frequencies of that molecule. In the present case, however, the assignment of the lowest frequencies (and most of the higher ones as well) is essentially the same for the D_4 and D_{2d} structures. Hence the fact that the measured heat capacity curve can be reproduced with the use of the D_4 assignment is no argument in favor of this structure. The values obtained in this calculation are listed in Table II along with the observed values.[5] The parameters used in the calculation, in addition to the frequencies of cycloöctatetraene from reference 3, are: $\theta = 125°$, the lattice expansion constant $a = 7.96 \times 10^{-3}$ and the vibrational expansion constant $b = 6.5 \times 10^{-4}$.

TABLE II

THE HEAT CAPACITY OF CRYSTALLINE CYCLOÖCTATETRAENE

T, °K.	C_p (calcd.)	C_p (obs.)[5]	T, °K.	C_p (calcd.)	C_p (obs.)[6]
10	0.47	...	140	19.82	19.73
20	2.93	2.98	150	20.87	20.73
30	5.78	5.70	160	21.80	21.73
40	7.94	7.82	170	22.85	22.74
50	9.56	9.46	180	23.80	23.76
60	10.89	10.87	190	24.82	24.82
70	12.11	12.17	200	25.89	25.90
80	13.37	13.40	210	27.00	27.00
90	14.52	14.57	220	28.03	28.11
100	15.63	15.64	230	29.03	29.26
110	16.72	16.67	240	30.15	30.45
120	17.78	17.70	250	31.18	31.63
130	18.82	18.73			

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[11] In discussion with the authors, Prof. B. D. Saksena has suggested that the double-bond mode whose frequency lies at 1651 cm.$^{-1}$ might be more effective than the 194 cm.$^{-1}$ vibration. This is possibly the case. In either event, there seems to be ample justification for regarding the interconversion as rapid.

[12] Lord and Andrews, *J. Phys. Chem.* **41**, 149 (1937).

[13] Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937).

Prior to the publication of the experimental heat capacity data, we had made an attempt to calculate the heat capacity curve. For this purpose we had estimated $\theta = 106$, $a = 8.9 \times 10^{-3}$ and $b = 6 \times 10^{-3}$. These parameters are somewhat in error, particularly the last one, and as a result the heat capacity curve was rather poorly reproduced below 80°K., where the heat capacity is most sensitive to θ, and especially above 180°, where it is most sensitive to the value of b. In the range 89–180°, the deviations were of the order of 1–4%.

Thermodynamic Functions for Some Reactions of Cyclooctatetraene

Another possibility for checking the structural basis of a vibrational assignment exists in the thermodynamic functions as determined from chemical equilibria. Unfortunately the same situation that gives rise to equivalent entropy values for the D_4 and D_{2d} structures operates to make it possible to explain experimental values of the free-energy and other thermodynamic quantities equally well on the basis of either structure. Regardless of this fact, the calculated values of these quantities may be of use in connection with the reactions of cycloöctatetraene, and we have therefore calculated equilibrium constants and related functions for several gas reactions involving the molecule.

The values of ΔH_f^0, ΔS_f^0 and ΔF_f^0 for the formation of cycloöctatetraene from its elements in their standard states at various temperatures are listed in Table III. These values were obtained from the heat of formation of liquid cycloöctatetraene[4] at 298.16°K., the heat of vaporization[5] at 298.16°K. (10.3 ± 0.075 kcal./mole) and the heats of formation and entropies of graphite and hydrogen in their standard states.[14]

TABLE III

THERMODYNAMICS OF FORMATION OF CYCLOÖCTATETRAENE VAPOR

T, °K.	ΔH_f^0, kcal.	ΔF_f^0, kcal.	ΔS_f^0, e.u.
298.16	71.12	88.40	−57.96
400	69.75	94.53	−61.95
500	68.68	100.82	−64.28
600	67.84	107.36	−65.87
700	67.13	114.05	−67.03
800	66.70	120.75	−67.56
900	66.32	127.56	−68.03
1000	66.18	134.33	−68.15

The equilibrium constants for some vapor-phase cycloöctatetraene reactions are given in Table IV. K_1 is the constant for the formation of one mole of cycloöctatetraene from four moles of acetylene, K_2 for formation from one mole of benzene and one mole of acetylene, and K_3 for isomerization to styrene. The necessary thermodynamic quantities for Table IV were obtained for acetylene and benzene from reference 14, and for styrene from Beckett and Pitzer.[15]

TABLE IV

EQUILIBRIUM CONSTANTS FOR SOME CYCLOÖCTATETRAENE REACTIONS

T, °K.	K_1	10^6K_2	K_3
298.16	7.1×10^{81}	40.7	2.24×10^{27}
400	3.55×10^{54}	11.5	4.47×10^{20}
500	2.95×10^{38}	5.37	5.13×10^{16}
600	5.01×10^{27}	3.27	1.26×10^{14}
700	9.55×10^{19}	2.29	1.74×10^{12}
800	1.58×10^{14}	1.74	6.61×10^{10}
900	5.25×10^{9}	1.51	5.25×10^{9}
1000	1.39×10^{6}	1.35	6.77×10^{8}

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(14) American Petroleum Institute Project 44, U. S. National Bureau of Standards, Washington 25, D. C., "Selected Values of Chemical Thermodynamic Properties."

(15) Beckett and Pitzer, THIS JOURNAL, **68**, 2313 (1946).

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High-temperature Heat Contents of Ferrous Oxide, Magnetite and Ferric Oxide[1]

BY J. P. COUGHLIN, E. G. KING AND K. R. BONNICKSON

High-temperature heat-content measurements of ferrous oxide, magnetite and ferric oxide were conducted from 298.16°K. to the respective temperatures, 1784, 1825 and 1757°K. One heat-capacity anomaly was found for magnetite and two for ferric oxide. The heat of fusion of ferrous oxide ($Fe_{0.947}O$) was determined. A table of heat content and entropy increments above 298.16°K. is given and heat content equations are derived.

Introduction

Despite the great importance of the oxides of iron, high-temperature heat-content data have not been available for ferrous oxide above 1173°K., for magnetite above 1273°K. or for ferric oxide above 1097°K. The only previous work on ferrous oxide is that of White,[2] who made determinations at only two temperatures, 973 and 1173°K. Magnetite was studied by Esser, Averdieck and Grass,[3] Roth and Bertram,[4] Weiss and Beck,[5] and Weiss, Piccard and Carrard.[6] Brown and Furnas,[7] Kolossowsky and Skoulski,[8] and Roth and Bertram[4] measured ferric oxide. The results for the latter two substances contain large discrepancies.

This paper reports the results of high tempera-

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(1) Not subject to copyright.

(2) White, THIS JOURNAL, **55**, 1047 (1933).

(3) Esser, Averdieck and Grass, *Arch. Eisenhüttenw.*, **6**, 298 (1933).

(4) Roth and Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

(5) Weiss and Beck, *Arch. sci. phys. nat.*, **25**, 529 (1098).

(6) Weiss, Piccard and Carrard, *ibid.*, **42**, 378 (1916); **43**, 22, 113, 199 (1917).

(7) Brown and Furnas, *Trans. Am. Inst. Chem. Eng.*, **18**, 309 (1926).

(8) Kolossowsky and Skoulski, *Bull. soc. chim. France*, **47** 136 (1930).