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Tetraethyllead. Vibrational assignment and chemical thermodynamic properties[a]

D. W. SCOTT

Bartlesville Energy Research Center, Bureau of Mines,
U.S. Department of the Interior, Battlesville, Oklahoma 74003, U.S.A.

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Vapor-state chemical thermodynamic properties were calculated for tetraethyllead. To that end, a molecular-vibrational analysis was used to estimate the unobserved C—Pb—C bending fundamentals, and a treatment of vapor-pressure data by currently available methods was used to estimate the enthalpy and entropy of vaporization.

1. Introduction

This work arose out of a thermodynamic study of alkane hydrocarbons with branching at a quaternary carbon atom. Comparison calculations were desirable for a structurally related compound with branching at a quaternary atom other than carbon. Tetraethyllead, with branching at a quaternary lead atom, was selected for that purpose because of the availability of the necessary thermodynamic and spectroscopic data. As the results for tetraethyllead may be of interest in themselves, independently of the problem that prompted the study, they are presented here.

2. Vibrational assignment

A vibrational assignment was needed for the statistical-thermodynamic calculations. Most of the assignment was available already from the thorough study of the infrared and Raman spectra reported by Jackson and Nielsen.(1) However, values of the thermodynamically important C—Pb—C bending fundamentals were lacking. To estimate those fundamentals, and to establish the remainder of the assignment more firmly, a molecular-vibrational analysis was carried out. The V_d conformation was selected because of its high symmetry. Force constants for the central PbC_4 part of the molecule were transferred from earlier work on tetramethyllead,(2) force constants for the ethyl groups were transferred from earlier work on aliphatic sulfur compounds,(3) and five additional force constants for the $Pb—CH_2—C$ group were adjusted to give the best least-squares fit to the observed wavenumbers. As the resulting force field probably is not transferable, the calculations are not reported in detail, and only the calculated values of the wavenumbers are listed in table 1 for comparison with the observed values. The results show that the a_2 fundamentals, inactive for V_d symmetry,

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TABLE 1. Observed and calculated wavenumbers σ of tetraethyllead

σ (obs.)/cm^{-1}	σ (calc.)/cm^{-1}	Δ/cm^{-1}	σ (obs.)/cm^{-1}	σ (calc.)/cm^{-1}	Δ/cm^{-1}
	a_1			b_2	
2940	2955	−15	2940	2955	−15
2918	2927	−9	2910	2927	−17
2860	2862	−2	2878	2862	16
1458	1450	8	1460	1450	10
1424	1425	−1	1427	1425	2
1373	1363	10	1377	1363	14
1164	1177	−13	1154	1176	−22
1014	1025	−11	1013	1025	−12
931	917	14	936	917	19
443	438	5	461	457	4
213	219	−6	213	219	−6
—	64.0	—	—	75.7	—
	b_1			e	
2960	2982	−22	2960	2982	−22
2940	2955	−15	2940	2955	−15
1458	1449	9	2940	2955	−15
1225	1245	−20	2910	2926	−16
958	946	12	2878	2862	16
674	676	−2	1460	1450	10
(≈107) [a]	108.9	—	1460	1449	11
			1427	1424	3
	a_2		1377	1363	14
—	2982	—	1227	1245	−18
—	2955	—	1154	1176	−22
—	1449	—	1013	1022	−9
—	1244	—	959	946	13
—	945	—	936	917	19
—	673	—	667	677	−10
			461	459	2
			243	228	15
			—	99.9	—

[a] Not used in adjustment of force constants.

must nearly coincide with their b_1 counterparts. The results also provide satisfactory estimates of the C—Pb—C bending fundamentals, at least in a statistical sense; if some of them are calculated too low, the others will be calculated too high in a nearly compensating fashion. Of course, experimental values from vapor-state far-infrared and Raman studies would be preferable, but they would be difficult to obtain because of tetraethyllead's low vapor pressure and thermal and photochemical instability.

3. Entropy and enthalpy of formation for the vapor state

Values of the entropy and of the enthalpy of formation for the liquid state have been reported.(4) To convert those values to the vapor state, the required values of the entropy and enthalpy of vaporization were estimated from vapor pressures.

Vapor pressures were available from three sources: (a) Buckler and Norrish,(5) who reported values in the low-pressure range determined by a Bourdon gauge method; (b) Jones *et al.*,(6) who reported values at somewhat higher pressures determined by a boiling temperature method; and (c) unpublished results obtained in the Ethyl Corporation laboratories. These last were mainly values obtained by boiling temperature methods for temperatures up to the normal boiling temperature, but included two values at lower pressures determined by a gas-saturation method.

All of the data, after elimination of a few that had excessive deviations, were used to derive a Cox vapor-pressure equation by a weighted least-squares method. As preliminary inspection showed that the scatter was about *three* times that expected from the original investigators' estimates of their precision, the effective uncertainty δ in pressure used for weighting purposes was taken to be

$$\delta = 3\{\delta_p^2+\delta_T^2(\mathrm{d}p/\mathrm{d}T)^2\}^{1/2},$$

in which δ_p and δ_T are the original investigators' estimates of their precision in measurement of pressure and temperature. The equation so obtained is:

$$\log_{10}(p/760\ \mathrm{Torr}) = \log_{10}(p/101.325\ \mathrm{kN\,m^{-2}}) = A(1-\Phi/T), \qquad (1)$$

in which

$$\log_{10} A = a+bT+cT^2;$$

and

$$\Phi = (470.27\pm3.08)\ \mathrm{K}; \qquad a = 0.99981\pm0.11670;$$
$$b = (1.2815\pm0.7077)\times10^{-3}\ \mathrm{K^{-1}}; \qquad c = (1.561\pm1.148)\times10^{-6}\ \mathrm{K^{-2}}.$$

The statistical uncertainties in the constants are those given by the variance-covariance matrix. These statistical uncertainties show that the data do justify use of a four constant equation, but just barely.

Figure 1 is a deviation plot of the vapor pressures with respect to equation (1), in which the weighted residuals are shown as a function of temperature. This method of plotting, besides displaying the actual quantities, the sum of the squares of which was minimized, also allows vapor pressures differing widely in magnitude or relative accuracy or both to be reduced to a common basis.

Equation (1) was used to calculate the enthalpy of vaporization at 298.15 K by means of the Clapeyron equation. Formally, an estimate of $-12\ \mathrm{dm^3\,mol^{-1}}$ for the pressure-explicit second virial coefficient B_p was used, although at the low pressure the effects of gas imperfection are scarcely significant. The calculations of the entropy and of the enthalpy of formation of the vapor are summarized in table 2; the compression term in the entropy of vaporization was obtained by use of equation (1).

Since the enthalpy of vaporization and entropy of vaporization and compression were evaluated from relatively imprecise vapor pressures, realistic estimates of uncertainty were desirable and were obtained by statistical analysis. For the enthalpy of vaporization, the quantity, $\delta(\Delta H_\mathrm{v})$, is given by:

$$\begin{aligned}\delta(\Delta H_\mathrm{v}) = \{&(\partial\Delta H_\mathrm{v}/\partial\Phi)^2\delta_\Phi^2+(\partial\Delta H_\mathrm{v}/\partial a)^2\delta_a^2+(\partial\Delta H_\mathrm{v}/\partial b)^2\delta_b^2+(\partial\Delta H_\mathrm{v}/\partial c)^2\delta_c^2\\ &+2(\partial\Delta H_\mathrm{v}/\partial\Phi)(\partial\Delta H_\mathrm{v}/\partial a)\delta_{\Phi a}+2(\partial\Delta H_\mathrm{v}/\partial\Phi)(\partial\Delta H_\mathrm{v}/\partial b)\delta_{\Phi b}\\ &+2(\partial\Delta H_\mathrm{v}/\partial\Phi)(\partial\Delta H_\mathrm{v}/\partial c)\delta_{\Phi c}+2(\partial\Delta H_\mathrm{v}/\partial a)(\partial\Delta H_\mathrm{v}/\partial b)\delta_{ab}\\ &+2(\partial\Delta H_\mathrm{v}/\partial a)(\partial\Delta H_\mathrm{v}/\partial c)\delta_{ac}+2(\partial\Delta H_\mathrm{v}/\partial b)(\partial\Delta H_\mathrm{v}/\partial c)\delta_{bc}\}^{1/2}, \qquad (2)\end{aligned}$$

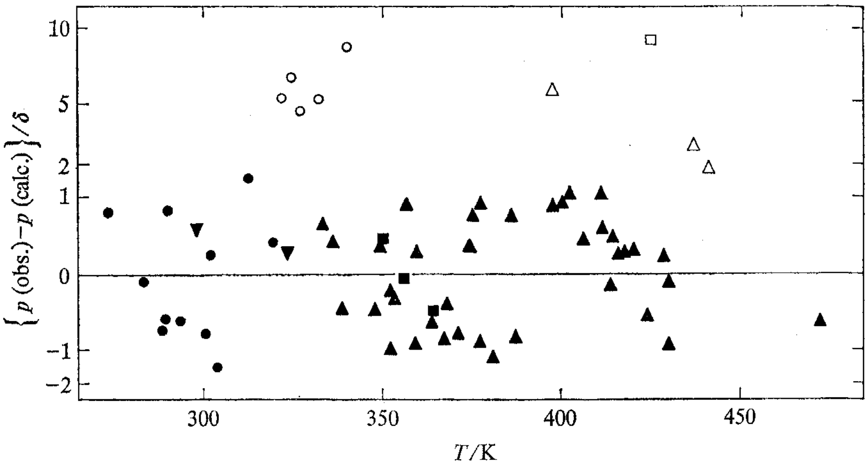

FIGURE 1. Deviation plot of vapor-pressures for tetraethyllead, showing weighted residuals with respect to equation (1) as a function of temperature. ●, Buckler and Norrish;[5] ■, Jones *et al.*;[6] ▲, Ethyl Corp., unpublished, boiling temperature methods; ▼, Ethyl Corp., gas-saturation method. Open symbols, data excluded from the least-squares adjustment because of excessive deviations.

TABLE 2. Entropy and enthalpy of formation of tetraethyllead in the vapor state ($\mathrm{cal_{th}} = 4.184$ J)

S_{satd} (liquid, 298.15 K)/$\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	111.9 ± 0.2
$(\Delta H_v/T)$/$\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$: $13.3_6 \times 10^3/298.15$	44.8 ± 1.5
Compression: $(R/\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}) \ln(0.385_1/760)$	−15.1 ± 0.0
Gas imperfection:	0.0 ± 0.0
S°(vapor, 298.15 K)/$\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	141.6 ± 1.6
ΔH°(liquid, 298.15 K)/$\mathrm{kcal_{th}\,mol^{-1}}$	12.6 ± 0.6[a]
ΔH°(vaporization, 298.15 K)/$\mathrm{kcal_{th}\,mol^{-1}}$	13.4 ± 0.5
ΔH°(vapor, 298.15 K)/$\mathrm{kcal_{th}\,mol^{-1}}$	26.0 ± 0.8

[a] Corrected to the currently accepted values of the enthalpy of formation of HNO_3 (in $30H_2O$), $Pb(NO_3)_2$(c), H_2O(l), and CO_2(g);[7] uncertainty given does not include uncertainty in these auxiliary thermochemical data.

in which $\delta^2_{\Phi}, \ldots \delta_{bc}$, are the elements of the variance-covariance matrix obtained in deriving equation (1). The quantity $\delta(\Delta H_v)$ accounts only for the effects of random error in the vapor pressure data. To be conservative, and to include some provision for systematic error, the uncertainty in the enthalpy of vaporization as given in table 2 was taken to be $2\delta(\Delta H_v)$ and in the entropy of vaporization was taken to be $2\delta(\Delta H_v)/T$. An analogous calculation for the entropy of compression showed that $2\delta(R\ln(p/760\ \mathrm{Torr}))$ was small enough to be neglected.

TABLE 3. Chemical thermodynamic properties of tetraethyllead in the ideal gas state ($\mathrm{cal_{th}} = 4.184$ J)

T/K	$-\{G°(T)-H°(0)\}/T$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$\{H°(T)-H°(0)\}/T$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$\{H°(T)-H°(0)\}$ / $\mathrm{kcal_{th}\,mol^{-1}}$	$S°$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$C_p°$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$\Delta H_f°$ [a] / $\mathrm{kcal_{th}\,mol^{-1}}$	$\Delta G_f°$ [a] / $\mathrm{kcal_{th}\,mol^{-1}}$	$\log_{10}K_f°$ [a]
0	0	0	0	0	0	$39._8$	$39._8$	$-\infty$
200	$95._5$	$27._1$	5.4_2	$122._6$	$41._5$	$29._8$	$66._1$	$-72._2$
273.15	$104._7$	$32._2$	8.8_0	$136._9$	$51._1$	$26._9$	$79._8$	$-63._9$
298.15	$107._6$	$34._0$	$10._1$	$141._6$	$54._6$	$26._0$	$84._7$	$-62._1$
300	$107._8$	$34._1$	$10._2$	$141._9$	$54._8$	$25._9$	$85._1$	$-62._0$
400	$118._6$	$40._9$	$16._4$	$159._5$	$68._1$	$22._5$	$105._3$	$-57._5$
500	$128._4$	$47._6$	$23._8$	$176._0$	$79._8$	$19._7$	$126._3$	$-55._2$
600	$137._7$	$53._8$	$32._3$	$191._5$	$89._7$	$17._5$	$147._9$	$-53._9$

[a] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction:

$$8\mathrm{C(c, graphite)} + 10\mathrm{H_2(g)} + \mathrm{Pb(c)} = \mathrm{C_8H_{20}Pb(g)}.$$

4. Chemical thermodynamic properties

Thermodynamic functions for tetraethyllead were calculated by standard methods. Vibrational contributions were obtained from the assignment of table 1; observed values were used if available, the a_2 fundamentals were taken the same as their b_1 counterparts, and the calculated values were used for the C—Pb—C bending fundamentals. The product of the three principal moments of inertia for overall rotation and the eight reduced moments of inertia for internal rotation were calculated from an assumed structure to be $3.354 \times 10^{-422}\ \mathrm{g}^{11}\ \mathrm{cm}^{22}$. The effective symmetry number for overall and internal rotation for the V_d conformation is $4 \times 3^4 \times 3^4 = 26244$. The first factor is the symmetry number for overall rotation; the second factor accounts for the fact that each ethyl rotation, by definition, is limited to $2\pi/3$ for a single conformation; and the third factor is for the methyl rotations.

The simplest possible model was adopted for the internal rotations. The ethyl rotations were taken to be free, by analogy with the methyl rotations of tetramethyl lead.(2) The methyl rotations were taken to be hindered by simple, threefold, cosine-type barriers of height $3.3\ \mathrm{kcal_{th}\ mol^{-1}}$, selected to give agreement with the experimental entropy value. The existence of other conformations of lower symmetry than V_d, and having the same energy on the assumption of free ethyl rotation, required a mixing term of $(R \ln 27)$ in $-\{G°(T) - H°(0)\}/T$ and $S°$.

The treatment just outlined was used to calculate the thermodynamic functions for 273.15 and 298.15 K and for five round temperatures between 200 and 600 K, so that values at intermediate temperatures could be obtained by five-point Lagrangian interpolation. The experimental value of the enthalpy of formation and values of the thermodynamic functions of C(c, graphite), H_2(g), and Pb(c)(6) were used to calculate the enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation at the same seven temperatures. The chemical thermodynamic properties are listed in table 3. The final digits, included for smoothness and internal consistency, are subscripted as a reminder that they are not necessarily significant. Although the values in table 3 are not as accurate as the ones normally compiled for lower molecular weight and chemically stable substances for which more extensive and more reliable experimental thermodynamic data are available, they should suffice for most practical chemical-thermodynamic calculations.

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