

Reaction between Bis(2,4-pentanedionato)lead(II) and Water Vapor: A Thermodynamic Study

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Evolved gas analysis Fourier transform infrared spectroscopy was used to investigate the high-temperature reaction between bis(2,4-pentanedionato)lead(II) and water vapor. 2,4-Pentanedione, acetone, and carbon dioxide were the principle gaseous products produced, and powder X-ray diffraction indicated that lead oxide and lead metal were the principle solid products formed. The equilibrium concentrations of all gaseous products and reactants were determined as a function of temperature and equilibrium constants were estimated from these data. The enthalpy of formation for bis(2,4-pentanedionato)lead(II) was determined to be -865 ± 10 kJ/mol.

Introduction

Chemical vapor deposition (CVD) processes are widely used in industry to generate thin films and to produce pure powders. Recently, Krisyuk et al.¹ determined that lead(II) diketonates could be used as lead transport agents in CVD processes to prepare compounds, such as lead-containing high-temperature superconductor films. Aoki et al.² used magnetron-discharge plasma CVD through low-pressure mixtures of bis(2,4-pentanedionato)lead(II), tris(2,4-pentanedionato)iron(III), and oxygen to prepare lead ferrite films exhibiting excellent magnetic characteristics. They also reported that discharging a mixture of bis(2,4-pentanedionato)lead(II) and tetra-*n*-propyl orthotitanate produced high-quality lead titanate films on silicon substrates.³

The physical properties and the chemical reactivity of bis(2,4-pentanedionato)lead(II) have not been extensively investigated and properties such as the enthalpy of formation and the enthalpy of sublimation, which are needed to model CVD processes,⁴⁻⁶ have not been determined. Wahlbeck⁷ has shown that DTA data can be used to estimate thermodynamic properties for thermal decomposition reactions. Evolved gas analysis can help determine the chemical reactions that are occurring.⁸ Preliminary investigations⁹ have shown

that coupling these methods provides a convenient method for estimating thermodynamic properties of metal organic compounds. This paper presents the results of an investigation that used this technique to explore the enthalpy of formation of bis(2,4-pentanedionato)lead(II).

Experimental Section

The apparatus used consists of a stainless steel IR cell which is coupled to a furnace assembly that can be heated at a constant rate and a Nicolet 740 FTIR that is used to monitor the evolved gases. The Nicolet 740 FTIR can collect and store one spectrum approximately every 2 s for reaction times up to 48 min. Each spectrum is obtained from 400 to 4000 cm^{-1} with four wavenumber resolution. The Aldrich IR spectral library is available on line to aid in the identification of the compounds produced during the reaction.

The stainless steel IR cell used has been described in detail previously.⁹⁻¹² Briefly, the cell was constructed from a MDC Corp. four-way cross vacuum flange (see Figure 1). One leg was used to connect the cell to the vacuum system. A stainless steel bellows valve between the cell and the vacuum system permitted experiments to be run while pumping on the cell (open cell) or while the cell was isolated from the vacuum (closed cell). Varying lengths of poly(tetrafluoroethylene) tubing could be inserted between the cell and the vacuum system. This permitted the effect of flow rate on the reaction to be investigated. Open-cell experiments produce DTA-like data, and closed-cell experiments give data resembling TGA experiments.^{8,9} The optical path was formed by using O-ring vacuum connectors to attach KBr windows to the two remaining opposing legs of the cell. The sample tube and the heating elements were connected to the remaining port using a Cajon 316 tube connector.

The sample tube was constructed from a 25 cm long piece of 9 mm glass tubing. Samples of 2,4-pentanedionatolead (0.1–0.2 g) were placed near the center of this tube and held in place using glass wool. The entrance of the tube was connected to a container of water. A Teflon needle valve controlled the water vapor flow entering the reaction region. The exit region of the sample tube was closed to a pinhole to restrict the flow out of the reaction region. Exiting water vapor

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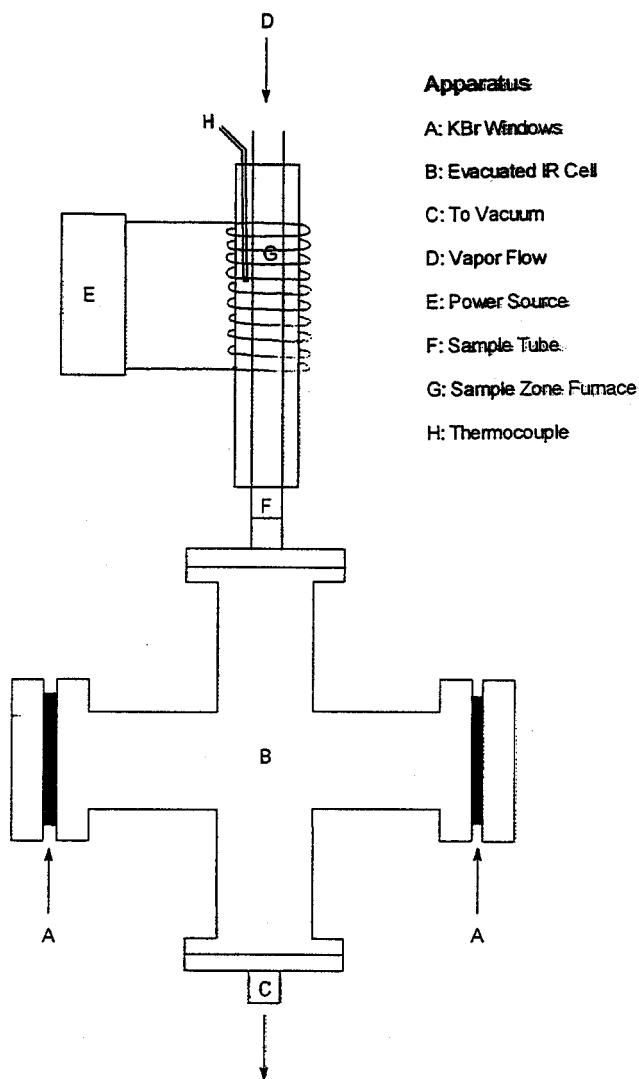


Figure 1. Schematic diagram of the stainless steel infrared cell used to investigate the reactions between 2,4-pentanedionatolead and water vapor.

pressures of a few pascals were used for most open-cell experiments. A static water vapor pressure of a few pascals was used in the closed-cell experiments.

The furnace assembly was constructed by wrapping a 12 mm Vycor tube with nichrome heating wire and thermal insulation. A Perkin regulated power supply controlled the power supplied to the furnace and provided heating rates between 6 and 10 °C/minute over the temperature range 323–573 K. The temperature of the sample was monitored using a chromel–alumel thermocouple connected to a Keithly digital thermometer.

The 2,4-pentanedionato lead used in this investigation was prepared by mixing approximately stoichiometric amounts of aqueous lead nitrate solution and sodium 2,4-pentanedionate. The sodium 2,4-pentanedionate was prepared by mixing a slight excess of 2,4-pentanedione with aqueous sodium hydroxide. The white solid formed when these solutions were mixed was suction filtered and air-dried. The IR spectrum of this compound showed only characteristic 2,4-pentanedionato complex bands and combustion analysis was consistent with the results expected for the bis(2,4-pentanedionato)lead(II). Prior to use, the compound was ground and further dried under vacuum in the apparatus.

Results and Discussion

Bis(2,4-pentanedionato)lead(II) largely sublimed and deposited on the cooler regions of the cell when a fresh

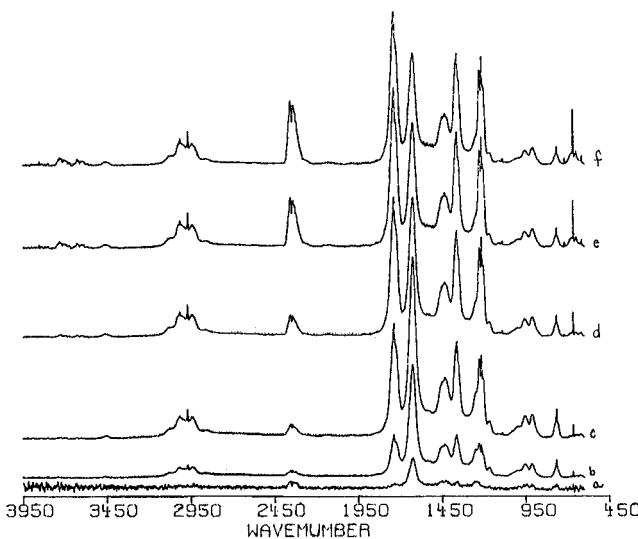


Figure 2. IR spectra observed for the thermal decomposition of 2,4-pentanedionatolead in vacuum. The decomposition temperatures were *a* = 350, *b* = 360, *c* = 395, *d* = 545, *e* = 585, and *f* = 625 K.

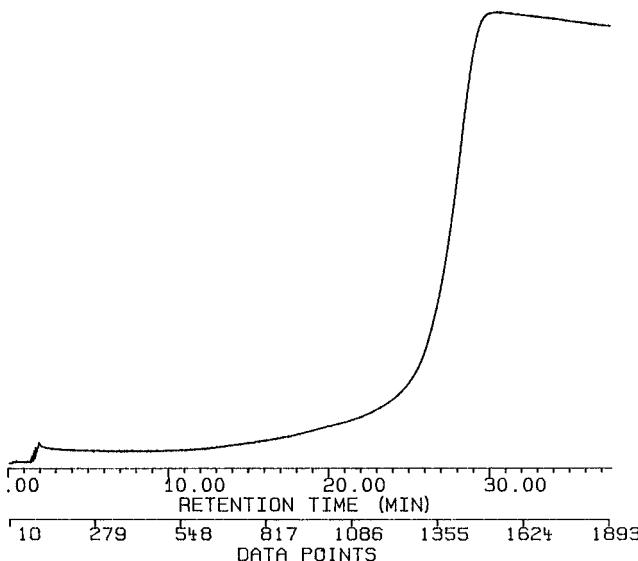


Figure 3. TGA-like EGA curve produced from the thermal decomposition of 2,4-pentanedionato lead in a water vapor atmosphere under closed-cell conditions.

sample was heated under vacuum with no added water vapor, but some chemical reaction did occur. The IR spectra of the evolved gases indicated that 2,4-pentanedione (1624 cm^{-1}), 2-propanone (1738 cm^{-1}), carbon dioxide (2357 cm^{-1}), and water vapor ($1500\text{--}1600\text{ cm}^{-1}$) were produced under these conditions (see Figure 2). X-ray diffraction analysis of the black residue left in the tube indicated that lead oxide and lead metal were formed during the reaction. Since water vapor and lead oxide were produced during the decomposition and previous investigations had indicated that metal oxides formed from the reaction between metal 2,4-pentanedionato complexes and water vapor,^{9,13,14} several experiments were performed adding water vapor to the cell. A typical EGA curve obtained in a water vapor atmosphere is presented in Figure 3. The chemigram

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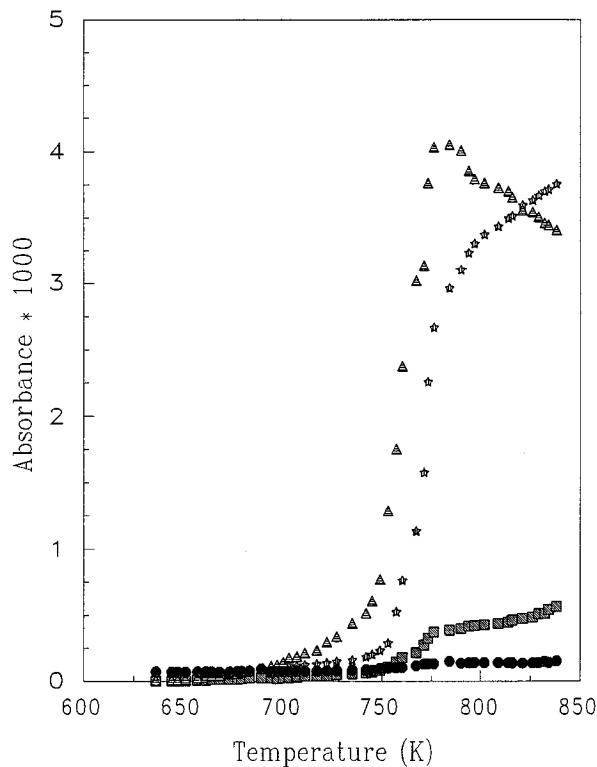
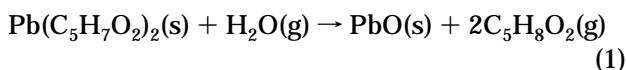


Figure 4. Absorbances of 2-propanone (★), 2,4-pentanedione (▲), carbon dioxide (■), and water vapor (●) as a function of temperature during the reaction between 2,4-pentanedionatolead and water vapor under closed cell conditions.

indicated that reaction occurred in one step until the sample residue turned from white to black. At this point, the total IR absorbance decreased slightly. IR spectra obtained at points along this curve showed that 2,4-pentanedione, 2-propanone, and carbon dioxide were the principle gaseous decomposition products. The 2,4-pentanedione and the acetone formed at different rates and their relative concentrations depended upon the amount of water vapor added to the cell. As shown in Figure 4 for a closed-cell experiment, the 2,4-pentanedione formed first when water vapor was added to the cell and increased following an exponential dependence. The 2-propanone showed a similar increase at approximately 20 K higher temperature. After the residue changed color suggesting that the lead complex was largely depleted, the intensity of the 2,4-pentanedione decreased while the intensity of the 2-propanone continued to increase (see Figure 4). Carbon dioxide began to increase in intensity at this point (~760 K).

Since the 2,4-pentanedione and the 2-propanone formed at different rates and the relative amounts of each changed as the experimental conditions changed, at least two distinct reactions are occurring. The exponential increase through the whole reaction range indicates zeroth order kinetics (near equilibrium conditions) are dominating. It is likely that the bis(2,4-pentanedionato)lead(II) reacts with water vapor to produce lead oxide and 2,4-pentanedione:



Assuming ideal behavior, i.e., the fugacity of each gaseous species is equal to the partial pressure of this species and the activity of each solid species is unity,

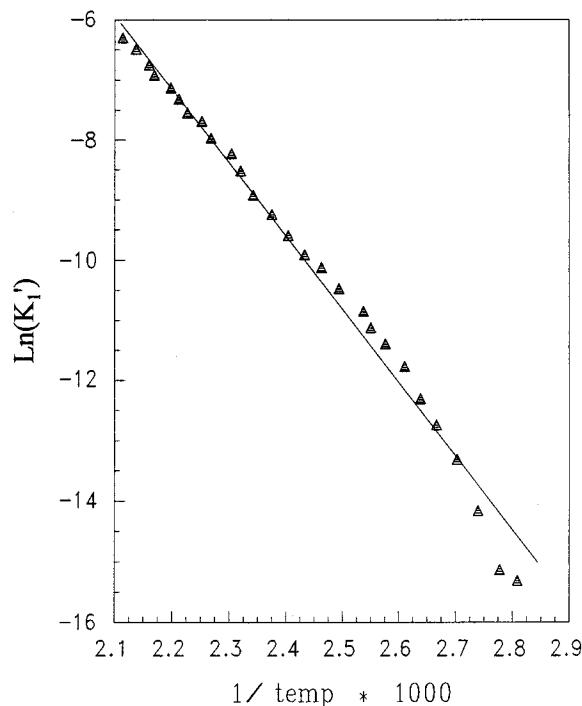


Figure 5. Plot of $\ln(K_1')$ vs 1/temperature based on the closed-cell conditions.

the equilibrium constant for this reaction is

$$K_1 = P(\text{C}_5\text{H}_8\text{O}_2)^2 / P(\text{H}_2\text{O}) \quad (2)$$

The partial pressure for each gaseous species is proportional to the sample absorbance

$$K_1' = (A(\text{C}_5\text{H}_8\text{O}_2)^2 / A(\text{H}_2\text{O}) T) \quad (3)$$

where K_1 and K_1' differ only by a constant factor.¹⁵ Values for K_1' were obtained for water vapor pressures that changed by a factor of 10, masses of bis(2,4-pentanedionato)lead(II) that varied by a factor of 2, and several orifice sizes and flow rates in open-cell flow experiments. No obvious differences in K_1' were observed by changing these conditions, and they also agreed with values obtained using closed cell experiments. Plots of $\ln(K_1')$ versus the reciprocal of the temperature (see Figure 5) were superimposable for several sets of experimental conditions and produced an average enthalpy of reaction of $+105 \pm 5 \text{ kJ/mol}$ for this reaction. Using this value for reaction 1 and literature values for the enthalpy of formation for PbO (-219.4 kJ/mol),¹⁶ H_2O (-241.4 kJ/mol),¹⁶ and $\text{C}_5\text{H}_8\text{O}_2$ vapor (-386.6 kJ/mol)¹⁷ and assuming that the enthalpy of reaction does not change with temperature, the enthalpy of formation for 2,4-pentanedionatolead is calculated to be $-855 \pm 10 \text{ kJ/mol}$.

A reaction that generated the 2-propanone and carbon dioxide is also occurring. Since the amount of 2,4-pentanedione decreases when the lead complex is exhausted and lead was observed in the products, it is possible that the lead oxide and 2,4-pentanedione

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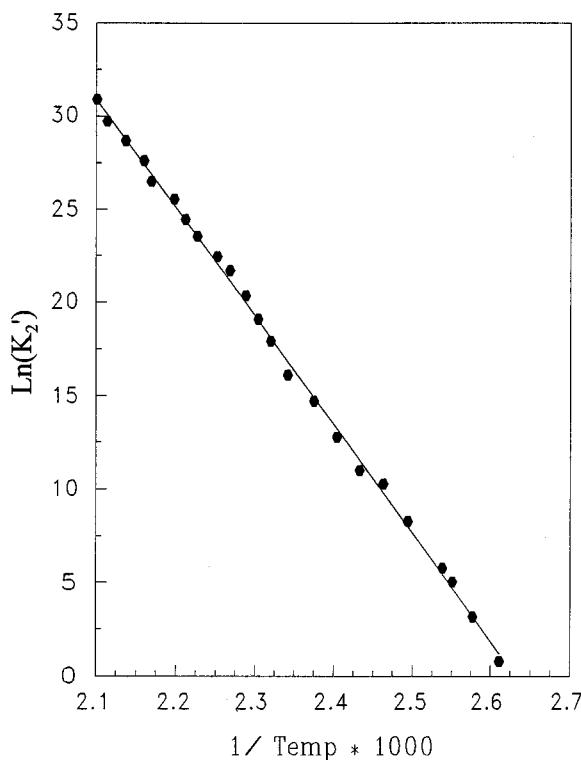
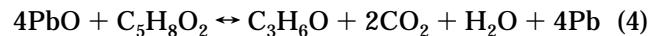
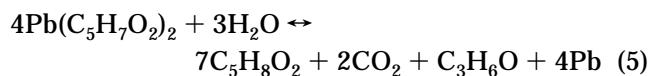


Figure 6. Plot of $\ln(K_2')$ vs 1/temperature based upon one closed cell experiment.

produced from reaction 1 react, i.e.



When coupled with reaction 1, the overall reaction for the low-temperature region would be



Assuming ideal behavior, the effective equilibrium constant for this reaction would be

$$K_2' = \frac{(\text{A}(\text{C}_5\text{H}_8\text{O}_2)\text{T})^7(\text{A}(\text{C}_3\text{H}_6\text{O})\text{T})(\text{A}(\text{CO}_2)\text{T})^2}{(\text{A}(\text{H}_2\text{O})\text{T})^3} \quad (6)$$

A typical plot observed for the $\ln(K_2')$ versus T^{-1} is shown in Figure 6. Although very good straight-line relationships were obtained for each individual experiment, uncertainties in measuring the absorbencies of all components led to larger run to run variation in the slopes than was observed for the plots relating to reaction 1. The average value determined for the enthalpy of reaction for reaction 5 was $+480 \pm 50$ kJ/mol. This provides a second measurement for the enthalpy of formation of $\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$. Using the enthalpies of formation cited previously and an enthalpy of formation for 2-propanone vapor of -217 kJ/mol,¹⁸ the enthalpy of formation for $\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$ determined from reaction 3 is -865 ± 20 kJ/mol; a value that is within the experimental error of the value obtained from reaction 1.

Another possible reaction is



When coupled with reaction 1, an additional equilibrium

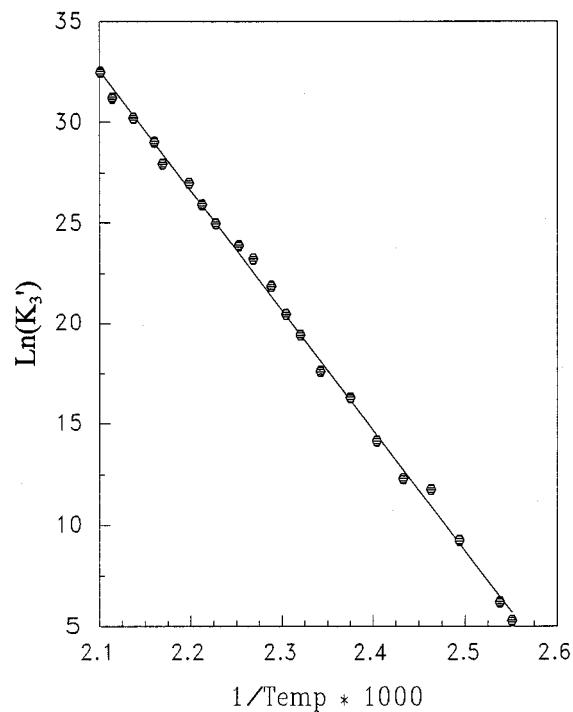
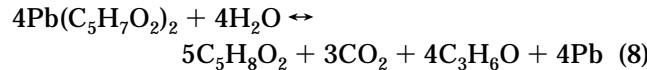


Figure 7. Plot of $\ln(K_3')$ vs 1/temperature using the TGA-like data.

reaction is possible:



The effective equilibrium constant for this reaction is $K_3' =$

$$(\text{A}(\text{C}_5\text{H}_8\text{O}_2)\text{T})^5(\text{A}(\text{C}_3\text{H}_6\text{O})\text{T})^4(\text{A}(\text{CO}_2)\text{T})^3/(\text{A}(\text{H}_2\text{O})\text{T})^4 \quad (9)$$

This reaction also produced good Van't Hoff plots (see Figure 7) that indicated an enthalpy of reaction of $+480 \pm 40$ kJ/mol. This produced an enthalpy of formation for $\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$ of -875 ± 25 kJ/mol.

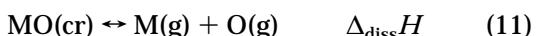
The enthalpies of formation for bis(2,4-pentanedione)-lead(II) calculated independently from the eqs 3, 6, and 9 agree to within the experimental uncertainty of the data. This agreement suggests that equilibrium has been obtained in the reaction region and that the average of these measurements, -865 ± 10 kJ/mol, should be a reasonable estimate for the enthalpy of formation for this compound. The slight differences in these values suggest that some nonideality corrections are needed before the exact value is determined. The data were also used to calculate the enthalpy of reaction for reactions 4 and 7. The values determined (Δ_rH of $+55 \pm 50$ and $+49 \pm 50$ kJ/mol) for reactions 4 and 7, respectively) compare to expected values of $+20$ and -10 kJ/mol, respectively. Both experimental values are more positive than expected. Although this could indicate that the system had not attained equilibrium, this does not seem likely since the deviation indicates that the products are in excess. It is possible that a homogeneous reaction such as



could be occurring in the cooler regions of the cell. This reaction is slightly exothermic and would produce the

observed deviation. However, heating mixtures of 2,4-pentanedione and water vapor produced no observable reaction, and this reaction would be expected to produce more disagreement in the calculated enthalpies of formation of the bis(2,4-pentanedione)lead(II) from the three equations used. It is more likely that the approximations used to calculate each enthalpy of reaction do not hold exactly. Corrections for activity and fugacity and corrections for the temperature dependence of the enthalpies of formation used to determine the enthalpies of reaction could easily produce better agreement. In any case, some correction is needed before an exact value for the enthalpy of reaction for the 2,4-pentanedionato lead is obtained. The agreement between the three measurements suggests that this correction will be small. If as found for reactions 4 and 7, the determined enthalpies of reaction are too positive, the enthalpy of formation determined for the 2,4-pentanedionato lead represents a lower limit to the true value.

Ribeiro da Silva et al.¹⁹ have suggested that the metal 2,4-pentanedionato enthalpies of formation mirror the average bond enthalpies of the corresponding metal oxides. They found a good linear relationship between the average bond enthalpy, calculated by dividing the enthalpy of dissociation



by the number of chemical interactions, and the enthalpy of dissociation for the systems that they examined. However, this relationship does not work well for lead or for several of the transition metals. A simpler approach would be to correlate the enthalpy of formation for the metal oxide to the enthalpy of formation for the 2,4-pentanedionato metal complex. This would require fewer parameters and would be easier to use. As shown in Figure 8, a good linear relationship between Δ_fH of the metal oxide and Δ_fH for the metal complexes for several transition metal and heavy-metal M^{2+} ions does exist. This correlation should provide reasonable estimates for the enthalpy of formation of the 2,4-pentanedionato metal(II) complexes that still have not been determined.

The reaction occurring when the 2,4-pentanedionato lead is depleted probably involves reactions between 2,4-pentanedione and PbO to form 2-propanone and carbon dioxide. Reactions 4 and 7 are possibilities, but further investigation will be needed before the chemistry occurring in this temperature range is firmly established.

Conclusions

The enthalpy of formation of bis(2,4-pentanedionato)-lead(II) has been established as being $-865 \pm 10 \text{ kJ/mol}$ from an EGA-FTIR investigation of the reaction between this compound and water vapor. Wahlbeck⁷ has shown that DTA data give good enthalpies of reaction when one of the product gases is used as a carrier gas. This investigation suggests that this method will also work when the reactant gases is used as a carrier gas, at least under restricted flow conditions. If

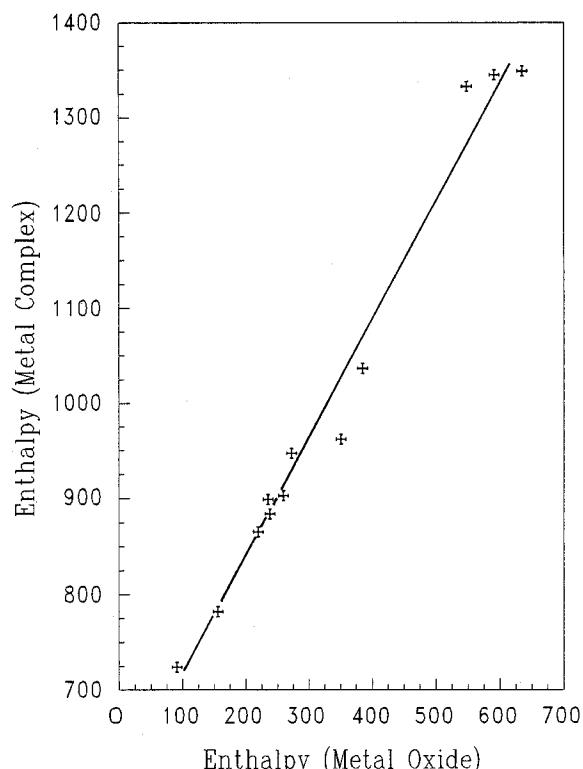


Figure 8. Plot of the enthalpy of formation for the metal(II) 2,4-pentanedionato complexes vs the enthalpy of formation for the metal oxides. The data used to make this plot are given in Table 1.

Table 1. Comparison of the Enthalpy of Formation of the Metal(II) Oxides to the Enthalpy of Formation for the Metal(II) 2,4-Pentanedionato Complexes (All Values in kJ/mol)

metal	Δ_fH (MO)	Δ_fH (M complex)	ref ^a
Hg	-91	-724	19, 19
Cu	-156	-782	15, 20
Pb	-219	-865	15, T. W.
Ni	-235	-899	19, 20
Co	-238	-884	15, 20
Cd	-259	-903	19, 19
Fe	-272	-947	15, 20
Zn	-351	-962	19, 19
Mn	-385	-1037	21, 20
Ba	-548	-1333	19, 19
Sr	-591	-1345	19, 19
Ca	-635	-1349	19, 19

^a The values given in this table are from the references cited. The first number is the reference for Δ_fH (MO).

so, then this will be an effective method for determining reaction enthalpies for organometallic and metal organic compounds.

A very good linear relationship has been established between the enthalpy of formation of the bis(2,4-pentanedionato)metal(II) complexes and the enthalpy of formation of the metal(II) oxides. This relationship should provide a good way of estimating the enthalpy of formation for these complexes. However, corrections for the temperature dependencies and the fugacities are needed before the true value can be obtained.

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