[CONTRIBUTION FROM THE UNIVERSITY OF BRITISH COLUMBIA]

A Spectrophotometric Study of the Stability of Lead(IV) in Hydrochloric Acid Solutions[1]

BY H. G. HEAL AND JOHN MAY

RECEIVED AUGUST 26, 1957

The absorption spectra of lead(IV) solutions are described. Equilibrium constants for the lead(IV)–lead(II)–chlorine system in hydrochloric acid solutions of 0.10 to 1.00 *N* concentration, at 19.5 and 25°, are reported, as well as specific rates for the decomposition of lead(IV) in 1.00 *N* hydrochloric acid at several temperatures.

Introduction

Wescott[2] studied the equilibrium between lead(IV), lead(II) and chlorine in hydrochloric acid solutions saturated with lead(II) chloride, by means of chemical analysis. He concluded that lead(IV) takes the form of the ion $PbCl_5^-$ in such solutions. His work was done before absorption spectroscopy had come into general use for studying the constitution of solutions, before it had become usual in equilibrium studies to take account of, or eliminate, the effect of varying ionic strength, and at only one temperature (25°). We have studied this equilibrium by making use of the previously undescribed ultraviolet absorption of lead(IV), and have determined equilibrium constants at 19.5 and 25.0°. We also give some data on rates of decomposition of lead(IV) at several temperatures near room temperature, which have not been reported previously. All our measurements were performed with solutions in 1.00 *N* hydrochloric acid, 1.00 *N* perchloric acid, or mixtures of these at a total concentration of 1.00 *N*. The results show that lead(IV) exists in at least two forms in solution, but support Wescott's conclusion about the predominant form in hydrochloric acid. Our investigation was of an exploratory character only, and has revealed a need for further work which we are not in a position to undertake at present.

Cesium hexachloroplumbate(IV), Cs_2PbCl_6, was employed throughout as a source of lead(IV). It was preferred to the better known ammonium salt because of its superior keeping qualities (it is stable up to 250° and unaffected by moist air), and because in solutions of the ammonium salt there is a risk of a reaction between ammonium ion and the chlorine formed by decomposition of the hexachloroplumbate(IV), which would have made it difficult to obtain reliable equilibrium data. The measurements were all made in the concentration range 10^{-3} to 10^{-4} *M*, so that the small solubility of the cesium salt was no disadvantage.

Experimental

Cesium hexachloroplumbate(IV) was made by passing chlorine into a suspension of 0.5 g. powdered AR lead(II) chloride in a solution of 5 g. of AR cesium chloride in 6 ml. of water, at 100°. When all the lead(II) chloride had dissolved, the yellow microcrystalline precipitate of cesium hexachloroplumbate(IV) which had formed was filtered, washed well with 0.2 *N* hydrochloric acid saturated with chlorine, drained and dried in a vacuum desiccator. The oxidizing power of the product, when dropped into standard iron(II) solution, and its loss in weight on heating to 275°, were within 2% of the theoretical for Cs_2PbCl_6. The quantities, 3–30 mg., of the salt required for standard solutions (usually in volumes of 25 or 50 ml.) were weighed out directly by means of a semi-microbalance and dropped into acid of the final concentration required.

Redistilled water, redistilled reagent grade hydrochloric acid, and reagent grade 60% perchloric acid were employed in the solutions.

In all equilibrium and kinetic measurements, steps were taken to ensure that all the chlorine formed in the decomposition of lead(IV) remained in the solution. Solutions were prepared and stored in calibrated flasks which were filled completely and glass-stoppered, mixing being accomplished by shaking glass beads about in the flask. Optical cells were also filled so as to leave little or no air space, and promptly stoppered.

Spectra were plotted by means of a Cary model 14 recording spectrophotometer, using 1 cm. or 10 cm. quartz optical cells. The sample compartment was thermostated to ± 0.2°.

Equilibrium data were obtained at 19.5 and at 25°, by allowing standard cesium hexachloroplumbate(IV) solutions to stand in completely filled stoppered flasks for several hours at the appropriate temperature in darkness, then quickly measuring the residual lead(IV) concentration by means of the absorbance at 307 mμ. The results obtained were independent of the period of standing, between 2.25 and 16 hours.

Kinetic runs were carried out with solutions in the optical cells. In order to minimize temperature changes arising from the handling of cells and pouring of solutions at the beginning of the runs, the following procedure was adopted. Twenty-eight ml. of the acid to be used in the run was placed in a 10-cm. cell of 33.5-ml. capacity, and allowed to come to the temperature planned for the run. Meanwhile a standard cesium hexachloroplumbate(IV) solution of about 5×10^{-4} molar, in the same acid, was brought to the same temperature. Five ml. of this solution then was pipetted quickly into the cell, and mixed by rocking the small air bubble back and forth. The dilution of the already equilibrated solution shifted the equilibrium, causing more lead(IV) to decompose. The change in lead(IV) concentration was followed by measuring the absorbance at 307 mμ. It made no difference to the decomposition rate, or to the final equilibrium concentration of lead(IV), whether the cell was continuously illuminated with 307 mμ light throughout the run, or only briefly at intervals of several minutes.

Results

The Absorption Spectrum of Lead(IV).—Since lead(IV) in hydrochloric acid decomposes to a considerable extent even during the time required to make up a solution and scan the spectrum, a pure lead(IV) spectrum cannot be directly observed, and has to be deduced from the experimental spectra of mixtures of lead(IV) with lead(II) and chlorine. The spectra shown in Fig. 1 were arrived at by the following procedure.

To begin with, some method of finding the instantaneous lead(IV) concentration at each wave length of the spectrum was required. Figures 1 and 2 show that there is a peak in the lead(IV) spectrum (at 303 mμ in 0.1 *N* HCl–0.9 *N* $HClO_4$, and at 307 mμ in 1.0 *N* HCl) in a region where neither the Pb^{++} ion nor any of its chloro-complexes absorbs appreciably. The absorption of chlorine is also relatively weak at this wave length. The

---

[1] Part of this investigation was carried out by John May as one of the requirements for the Honours B. A. degree of the University of British Columbia.

[2] E. W. Wescott, THIS JOURNAL, **42**, 1335 (1920).

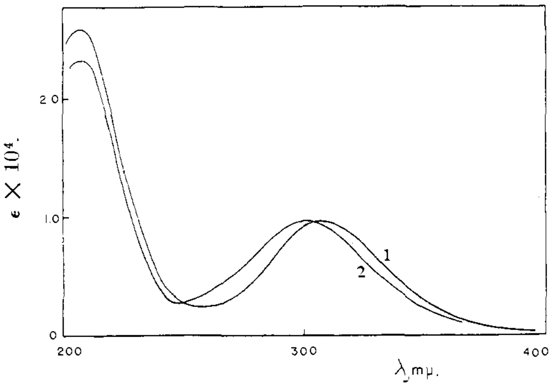

Fig. 1.—Calculated absorption spectra of lead(IV), at 19.5°: (1) in 1.00 *N* HCl; (2) in 0.10 *N* HCl–0.90 *N* $HClO_4$; ε = molar absorptivity, plotted on a linear scale.

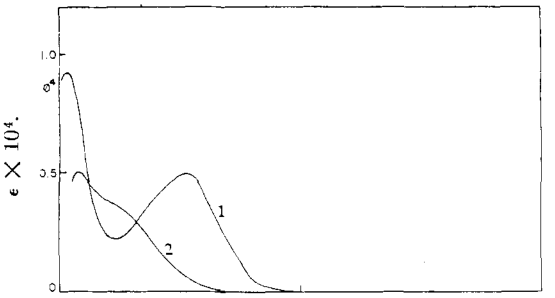

Fig. 2.—Measured absorption spectra of lead(II) at 19.5°: (1) in 1.00 *N* HCl; (2) in 0.10 *N* HCl–0.90 *N* $HClO_4$; ε = molar absorptivity, plotted on a linear scale.

height of this peak (duly corrected for absorption by chlorine) was therefore used as a measure of the lead(IV) concentration. The absolute value of ε, the molar absorptivity of lead(IV), at 307 mμ, was found in the first instance by plotting the decay of the peak against time, and extrapolating back to find the height at the time when the standard solution was mixed. There are several uncertainties in this extrapolation, and fortunately an independent check on the value of ε so obtained was available. The equilibrium ratio $[Pb(II)]\cdot[Cl_2]/[Pb(IV)] = K'$ (see next paragraph), calculated from the experimental data, can only be independent of the Pb(II)/Pb(IV) ratio if a correct value of ε is employed in the calculations. It was found in fact, that the value of ε at 307 mμ obtained as the mean of two back-extrapolations considered reliable, 0.97×10^4, did give K' values independent, within experimental error, of the Pb(II)/Pb(IV) ratio, for solutions of HCl concentration between 0.10 and 1.00 *N*, and at temperatures of 19.5 or 25°. It was therefore adopted. We consider that the value $\epsilon = 0.97 \times 10^4$ is probably reliable within 3 or 4% for the solutions with hydrochloric acid concentration 0.35 *N* and higher, but may be somewhat more in error than this for 0.1 *N* hydrochloric acid, since the spectrum at this concentration is appreciably different (Fig. 1), and our K' values for this concentration are not so consistent as at higher concentrations (Table I).

The spectrum of a partially decomposed solution of lead(IV) was plotted at a known rate of scanning. The rate of decline of absorbance at 307 mμ then was determined, and thence the instantaneous lead(IV) concentration at each of a series of wave lengths in the spectrum of the mixture. The initial lead(IV) concentration being known, also the stoichiometric relationship $Pb(IV) \rightarrow Pb(II) + Cl_2$, the instantaneous concentrations of lead(II) and chlorine at each wave length were calculated next. The absorptivity of lead(II) in acid of the same composition was separately measured (Fig. 2), and that of chlorine obtained from the data of Zimmerman and Strong.[3] The absorbance at each wave length due to lead(IV) was then calculated by subtracting the lead(II) and chlorine absorbances from the total absorbance at that wave length. This, together with the previously calculated lead(IV) concentrations, gave the absorptivities plotted in Fig. 1. Spectra were measured at 19.5° rather than 25°, because the lead(IV) decomposes inconveniently quickly at 25°. Zimmerman and Strong's data on the chlorine spectrum at 25° were assumed to be accurate enough at 19.5°.

There are no peaks in the visible spectrum, though concentrated lead(IV) solutions look pale yellow because of absorption in the tail of one of the ultraviolet bands: the ultraviolet spectrum shows two prominent peaks. The stronger, at 208 mμ, coincides almost exactly with similar peaks in the spectra of lead(II) in hydrochloric or perchloric acids. The other peak comes at just over 300 mμ. It appears to shift toward shorter wave lengths as the hydrochloric acid concentration is reduced, though the shift (307–303 mμ) between 1.00 and 0.10 *N* HCl is not pronounced. In 0.35 *N* hydrochloric acid the peak was found at about 306 mμ; the spectrum was not measured completely at this concentration. In 1.00 *N* perchloric acid with no added chloride, however, (Fig. 3), the peak appears to have shifted right down to 250 mμ approximately.

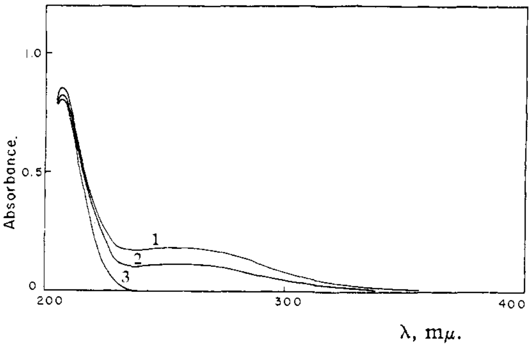

Fig. 3.—(1) Absorption spectrum of a partially decomposed solution of Cs_2PbCl_6 in 1.00 *N* $HClO_4$, initially 0.9×10^{-4} *M*. (2) The same solution nine minutes later. (3) 0.9×10^{-4} *M* $PbCl_2$ in 1.00 *N* $HClO_4$. (All spectra at 19.5°, solutions in 1 cm. cells.)

The Lead(IV)–Lead(II)–Chlorine Equilibrium.—One cannot write a single equation for this equilibrium, since lead(II) exists in hydrochloric acid solutions as a mixture of complexes containing

---

[3] G. Zimmerman and F. C. Strong, THIS JOURNAL, **79**, 2063 (1957).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE LEAD(IV)–LEAD(II)–CHLORINE EQUILIBRIUM

T = temp., °C.; N_1 = moles HCl/l., N_2 = moles $HClO_4$/l. C_1 = equilibrium moles Pb(IV)/l. × 10^4; C_2 = equilibrium moles Pb(II) or Cl_2/l. × 10^4; $K' = C_1^2/C_2$ (equilibrium constant).

T	N_1	N_2	C_1	C_2	K' × 10^3	Mean K' × 10^3
19.5 ± 0.3	1.00	Zero	1.06	3.57[a]	1.20	
			0.566	2.66	1.25	
			0.192	1.57	1.28	1.23 ± 0.06
			1.05	3.52[b]	1.18	
			0.54	2.50	1.17	
			0.25	1.79	1.29	
	0.70	0.30	1.26	5.24	2.19	
			0.741	4.11	2.28	2.26 ± 0.08
			0.211	2.21	2.31	
	0.35	0.65	1.43	10.9	8.33	
			0.997	9.05	8.21	8.3 ± 0.1
			.436	6.02	8.31	
	0.10	0.90	.230	19.7	169	
			.170	17.1	171	170 ± 10
			.083	12.9	201	
25.0 ± 0.2	1.00	Zero	.960	4.25	1.88	
			.580	3.29	1.86	1.88 ± 0.06
			.305	2.42	1.91	
	0.70	0.30	.604	4.44	3.27	3.3 ± 0.1
	.35	.65	.688	9.10	12.1	12.1 ± 0.4
	.20	.80	.723	17.3	41.6	41.6 ± 1.5
	.10	.90	.169	19.5	225	225 ± 15

[a] Solutions equilibrated 4 hours. [b] Solutions equilibrated 2.25 hours.

from one to four chloride ions with the uncomplexed ion,[4] chlorine exists partly as Cl_2 and partly as Cl_3^-,[3] while lead(IV) (as shown above) must be present as at least two species. Only the chlorine–trichloride ion equilibrium, of these three equilibria of complex formation, has been fully investigated. However, for any stated group of ionic species there will be an equilibrium equation of the form

$$\mathrm{Pb(II)} + Cl_2 + n\mathrm{Cl}^- \rightleftharpoons \mathrm{Pb(IV)}$$

including one atom each of Pb(II) and Pb(IV) and one molecule of chlorine (free or combined as Cl_3^-). Two such equations might, for example, be

$$PbCl^+ + Cl_2 + 2Cl^- \rightleftharpoons PbCl_5^-$$

and

$$PbCl_2 + Cl_2 + Cl^- \rightleftharpoons PbCl_5^-$$

For the very dilute lead solutions employed in this work, in which the relative concentrations of the different complexes of a given oxidation state are independent of the total concentration of that state, it follows that

$$\frac{[\text{total Pb(II)}][\text{total Cl}_2]}{[\text{total Pb(IV)}]} = K'$$

K' should not depend on any of the concentrations on the left-hand side, but will be a function of the chloride ion concentration. This relationship fits the experimental data well. From the practical standpoint, the most useful mode of presentation of the data seems to be as a series of K' values for various chloride ion concentrations. These are given in Table I.

The Rate of Decomposition of Lead(IV).—Standard kinetic treatment of the reversible reaction

$$\mathrm{Pb(IV)} \rightleftharpoons \mathrm{Pb(II)} + Cl_2$$

as a unimolecular reaction opposed by a bimolecular one leads to the expression

$$-kt = \frac{(C_0 - C_\infty)}{(C_0 + C_\infty)}\left\{\ln\frac{(C - C_\infty)}{\left(\frac{C_0^2}{C_\infty} - C\right)} + \ln\frac{\left(\frac{C_0^2}{C_\infty} - C_0\right)}{(C_0 - C_\infty)}\right\}$$

k = specific rate of forward reaction
C = instantaneous lead(IV) concn.
C_0 = initial lead(IV) concn.
C_∞ = final equilibrium lead(IV) concn.
t = time

This expression should hold as long as the chlorine formed in the decomposition is entirely retained in the solution, which was the case in these experiments. Actually, it fitted the experimental data very well, good straight line plots being obtained for

$$\log\frac{(C - C_\infty)}{\left(\frac{C_0^2}{C_\infty} - C\right)} \text{ against } t.$$

k values for 1.00 N HCl solutions, deduced from the gradients of these lines, are shown in Table II.

TABLE II

SPECIFIC RATES FOR THE DECOMPOSITION OF LEAD(IV) IN 1.00 N HYDROCHLORIC ACID

T, °C.	k[a]
24.7	0.1035
23.7	.0917
20.2	.0486
16.1	.0342

[a] k in minutes^{-1}.

A full study of the effect of chloride ion concentration upon the rate was not undertaken. However, some specific rate values for 1.00 N $HClO_4$ solutions were about twice those for 1.00 N HCl solutions at the same temperature.

Discussion

Figure 4 shows how K' varies with the chloride ion concentration, at constant ionic strength. From the equilibrium equations given in the foregoing paragraph it is to be expected that $K' = K''/[Cl^-]^{\bar{n}}$, where K'' is a constant independent of $[Cl^-]$, and $\bar{n}$ is the weighted average number of chloride ions required to convert lead(II) into lead(IV). The slope of the graphs of Fig. 4 at any point gives $\bar{n}$ at that particular chloride ion concentration. Now lead(II) in 0.10 N hydrochloric acid is known to exist largely as the complex $PbCl^+$, while complexes with more than one chloride ion become increasingly prevalent at higher chloride ion concentrations.[4] At $[Cl^-] = 0.10$ N, $\bar{n} = 2.3$ from Fig. 4. If the lead(IV) ion were mainly $PbCl_6^=$ in 0.10 N hydrochloric acid, as it is in the solid hexachloroplumbates(IV), three chloride ions would be involved in the principal equilibrium

$$PbCl^+ + Cl_2 + 3Cl^- \rightleftharpoons PbCl_6^=$$

and $\bar{n}$ should be about 3. In fact, $\bar{n}$ is nearer 2; this supports Wescott's belief that the main form

---

(4) H. Fromherz and K.-H.-Lih, *Z. physik. Chem.*, **A153**, 321 (1931); A. I. Biggs, H. N. Parton and R. A. Robinson, THIS JOURNAL, **77**, 5844 (1955).

of the lead(IV) ion in hydrochloric acid is $PbCl_6^-$, which would make the principal equilibrium in 0.10 *N* hydrochloric acid

$$PbCl^+ + Cl_2 + 2Cl^- \rightleftharpoons PbCl_6^-$$

The decrease in $\bar{n}$ to 1.7 in 1.00 *N* hydrochloric acid probably is caused by an increased contribution of equilibria involving higher chloro complexes of lead(II), such as $PbCl_2$ and $PbCl_3^-$.

There is a comparatively small change in the absorption spectrum of lead(IV) between 1.00 and 0.10 *N* hydrochloric acid, and a large change between 0.10 *N* and zero hydrochloric acid. A simple explanation of these facts is that lead(IV) may exist as two forms in equilibrium

$$PbCl_4 + Cl^- \rightleftharpoons PbCl_5^-$$

the equilibrium lying almost entirely to the right in 1.00 *N* hydrochloric acid, mainly to the right in 0.10 *N* hydrochloric acid, and mainly to the left in perchloric acid with no hydrochloric acid. More experimental work would be needed to show whether this suggestion is quantitatively reasonable.

The temperature coefficient of the rate of decomposition of lead(IV) in 1.00 *N* hydrochloric acid leads to an activation energy of 23 ± 5 kcal. per mole. This is consistent with a frequency factor of about 10^{13} per second, and a small entropy of activation.

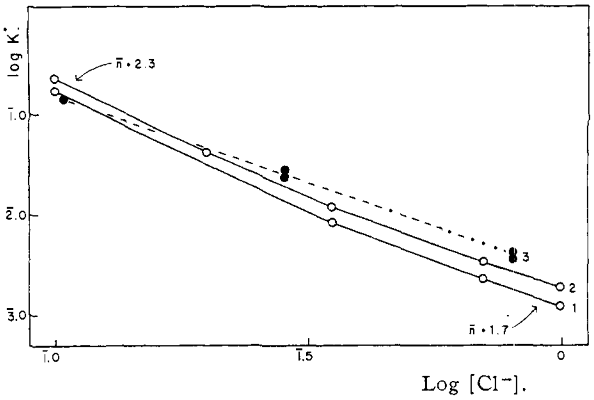

Fig. 4.—Variation of the equilibrium ratio *K'* with chloride ion concentration: (1) Our data at 19.5° (constant ionic strength = 1.00); (2) Our data at 25.0° (constant ionic strength = 1.00); (3) Calculated from Wescott's data (ionic strength varying, approximately equal to chloride ion concentration): temperature 25.0°. Concentrations in gram ions per liter. Slope = $\bar{n}$ = average number of chloride ions involved in conversion of lead(II) to lead(IV).

VANCOUVER 8, CANADA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Surface Catalysis of the Ortho- to Para-Conversion in Liquid Hydrogen by Paramagnetic Oxides on Alumina

BY CLARENCE M. CUNNINGHAM[1] AND HERRICK L. JOHNSTON

RECEIVED OCTOBER 8, 1957

The influence of surface concentration and magnetic moments of paramagnetic ions on the rate of ortho- to para-conversion in liquid hydrogen was investigated for several catalysts supported on alumina. It was found that the rate of conversion increased directly with the surface concentration and as the square of the magnetic moment of the paramagnetic ions on the surface of the alumina carriers. It was assumed that (a) the reaction took place only within the first adsorbed layer, (b) there was preferential adsorption of the orthohydrogen within the first adsorbed layer and (c) the reaction was first order with respect to the orthohydrogen concentration in the first adsorbed layer. The experimental rate results were fitted to the equation $(s - 1)(0.75)x + \ln 1/(1 - x) = skt$, where x is the fraction of orthohydrogen converted at time t, s is the separation coefficient and k is the first-order rate constant. The separation coefficient was calculated from the rate equation and was found to be 16 ± 3. This large separation coefficient combined with a very low rate of conversion of ortho- to parahydrogen on pure alumina surfaces suggests that alumina could be used at liquid hydrogen temperature to prepare pure orthohydrogen.

Introduction

Until the present time few investigations have been conducted of the heterogeneous ortho- to para-conversion in liquid hydrogen. Cremer and Polanyi[2] investigated the homogeneous conversion in liquid and solid hydrogen in the absence of a catalyst and found that the conversion was second order with respect to the concentration of orthohydrogen. In both liquid- and solid-phase reactions the rate constant was found to be independent of the temperature. Swenson[3] investigated the heterogeneous ortho- to para-conversion in liquid hydrogen on charcoal and silica gel and reported that the rate was first order with respect to the concentration of orthohydrogen.

The low temperature, or magnetic, mechanism for the ortho–para conversion in the gas phase has been understood for some time. A theoretical equation for the transition probability for conversion by collision with a paramagnetic substance was developed by Wigner.[4] Farkas and Sassche[5] found that both the homogeneous gas-phase conversion catalyzed by oxygen and other paramagnetic gases and the conversion catalyzed by paramagnetic ions in aqueous solution could be explained by the Wigner theory. Harrison and McDowell[6] modified the Wigner theory and applied it to the surface catalysis of the ortho- to para-conversion in hydrogen adsorbed on a paramagnetic surface at low pressures and liquid nitrogen tem-

---

[1] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma.

[2] E. Cremer and M. Polanyi, *Z. physik. Chem.*, **B21**, 459 (1933).

[3] C. A. Swenson, *J. Chem. Phys.*, **18**, 520 (1950).

[4] E. Wigner, *Z. physik. Chem.*, **B23**, 28 (1933).

[5] L. Farkas and H. Sassche, *ibid.*, **B23**, 1, 19 (1933).

[6] L. G. Harrison and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A220**, 77 (1953).