

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Ionization Constants of Osmic(VIII) Acid<sup>1</sup>

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Spectrophotometric measurements in potassium hydroxide solutions yield a value of  $1.0 \times 10^{-12}$  for apparent  $K_1$  and  $3 \times 10^{-15}$  for  $K_2$  of osmic(VIII) acid at 1.0  $M$  ionic strength and 25°. Determination of the distribution of osmium(VIII) between sodium hydroxide solutions and carbon tetrachloride give  $K_1(\text{apparent}) = 1.0 \times 10^{-12}$  and  $K_2 \geq 1 \times 10^{-15}$ . Since osmium tetroxide exists largely as such, and not as perosmic acid, in aqueous solutions the true value of  $K_1$  is greater than  $1.0 \times 10^{-12}$  and may be estimated as  $\sim 10^{-10}$ .

Yost and White<sup>2</sup> obtained the value  $8 \times 10^{-13}$  for the primary ionization constant of osmic(VIII) acid (usually called perosmic acid) from the distribution of osmium tetroxide between sodium hydroxide solutions and carbon tetrachloride at 25°. The chief aim in the present work was the determination of the secondary ionization constant, hitherto unreported. This required a value as exact as possible for the primary ionization constant, which therefore was redetermined. Values for both constants were obtained by two independent methods involving distribution and spectrophotometric measurements.

The composition of perosmic acid is not known.<sup>3</sup> The formula is frequently written as  $H_2OsO_6$ , chiefly for simplicity of representation. We shall represent the composition by the general formula  $H_{2n}OsO_{4+n}$  and assume that only one species of the undissociated acid, containing one Os atom per molecule, is present in the very dilute solutions used in this work.

The following expression can be derived for the distribution of osmium between an aqueous solution (w) and an immiscible organic solvent (o) at constant ionic strength as a function of the hydrogen ion concentration

$$\frac{P}{E} = 1 + \frac{K'_1}{[H^+]} + \frac{K'_1 K_2}{[H^+]^2} \quad (1)$$

where the symbols have the following meaning

$P$  = partition coefficient of osmium tetroxide

$$= \frac{[OsO_4]_o}{[OsO_4]_w + [H_{2n}OsO_{4+n}]_w} \quad (2)$$

$E$  = extraction coefficient (involving all forms of osmium in the aqueous phase)

$$= \frac{[OsO_4]_o}{[OsO_4]_w + [H_{2n}OsO_{4+n}]_w + [H_{2n-1}OsO_{4+n}]_w + [H_{2n-2}OsO_{4+n}]_w} \quad (3)$$

$K'_1$  = (apparent primary ionization constant)

$$= \frac{[H^+][H_{2n-1}OsO_{4+n}]_w}{[OsO_4]_w + [H_{2n}OsO_{4+n}]_w} \quad (4)$$

$$K_2 = \frac{[H^+][H_{2n-2}OsO_{4+n}]_w}{[H_{2n-1}OsO_{4+n}]_w} \quad (5)$$

$E$ , but not  $P$ , is a function of the hydrogen ion concentration.  $P$  is actually the apparent partition coefficient of osmium tetroxide, since some of it exists as the acid in aqueous medium. The rela-

tive amounts of  $OsO_4$  and  $H_{2n}OsO_{4+n}$  in water are not known, but the equilibrium doubtless lies toward the side of  $OsO_4$ . The first ionization constant is based on the sum  $[OsO_4]_w + [H_{2n}OsO_{4+n}]_w$  and is thus an apparent constant, which is denoted by the prime.

Partition measurements in acidic or neutral solutions give the value of  $P$ , in weakly basic solutions of an  $E$  leading to  $K'_1$ , and in more strongly basic solutions of an  $E$  leading to  $K_2$ .

**Apparatus.**—A Beckman model B spectrophotometer with 1-cm. Pyrex cells was used for optical density measurements (the DU model would have been more suitable but was not available).  $pH$  measurements were made with a Beckman model G  $pH$  meter with an alkaline glass electrode.

**Reagents.**—Osmium tetroxide, reagent quality, was used without further purification. Solutions in water were standardized by Klobbie's iodometric method in the absence of air and with starch as an external indicator.

Carbon tetrachloride, reagent quality, was refluxed successively with bromine water and sodium hydroxide solution and distilled after drying with Drierite.

Sodium hydroxide solutions prepared from an analytical reagent product and by electrolysis of sodium chloride gave identical results in distribution experiments with  $OsO_4$ . No indication of the presence of substances reducing Os(VIII) was found. The potassium hydroxide used was analytical reagent.

Sodium perchlorate was prepared by neutralizing reagent quality perchloric acid with sodium hydroxide.

## Experimental

**Partition Measurements.**—These were carried out by mechanically shaking 10 ml. of carbon tetrachloride with 20 ml. of aqueous solution in glass-stoppered bottles for 10 minutes, a period of time shown to be ample for attainment of equilibrium. Osmium was determined photometrically in an aliquot of each phase by the thiourea method (the carbon tetrachloride solution of osmium tetroxide was shaken with an acidified water solution of thiourea). Except in one series of determinations in the absence of added electrolyte, the ionic strength of the aqueous solution was maintained constant at 1.0  $M$  by addition of sodium perchlorate. The  $pH$  of the aqueous solution was obtained with a glass electrode after the shaking, and sodium ion corrections were made.

**Spectrophotometric Measurements.**—Values of the ratio  $[H_{2n-1}OsO_{4+n}]_w / \{ [OsO_4]_w + [H_{2n}OsO_{4+n}]_w \}$  were found from measurements of optical density of sodium hydroxide solutions of known  $pH$  at 420  $m\mu$ . At this wave length the equilibrium mixture of osmium tetroxide and the un-ionized acid absorbs but slightly at the low concentrations employed, whereas the univalent anion,  $H_{2n-1}OsO_{4+n}$ , absorbs strongly. Moreover, the divalent anion absorbs only slightly more strongly than the univalent anion at this wave length, so that below  $pH \sim 13$  a correction need not be applied for the effect of the former ion on the optical density.

To determine  $K_2$  spectrophotometrically, optical density measurements of osmium tetroxide in potassium hydroxide solutions were made at 360  $m\mu$ . At this wave length,  $\epsilon_2$  (of the secondary anion) is twice as great as  $\epsilon_1$  (of the primary anion).

(1) In part from the Ph.D. thesis of R. D. Sauerbrunn, 1952.

(2) D. M. Yost and R. J. White, *THIS JOURNAL*, **50**, 81 (1928). See also L. H. Anderson and D. M. Yost, *ibid.*, **60**, 1823 (1938), and L. Chugaev and A. J. Lukashuk, *Z. anorg. allgem. Chem.*, **172**, 223 (1928).

(3) Potassium and cesium salts of perosmic acid prepared by reaction of osmium tetroxide with very strong alkali hydroxide solutions were claimed to have the composition  $M_2[OsO_4(OH)_2]$  by F. Krauss and D. Wilken, *Z. anorg. allgem. Chem.*, **145**, 151 (1925). The 2:1 ratio of M to Os is doubtless correct but the remainder of the formula is uncertain.

**Results**

Values for the partition coefficient ( $P$ ) of osmium tetroxide between water and carbon tetrachloride are listed in Table I. Extraction coefficients ( $E$ ) for basic solutions at unit ionic strength are given in Table II, together with values of  $K_1'$  and  $K_2$  calculated by means of equation (1), with hydrogen ion activity substituted for  $[H^+]$ . The values for  $K_2$  can be only approximate, because they are obtained as a difference between two similar quantities, as shown by the following expression in which average values of  $P$ ,  $E$  and  $K_1'$  are used

$$K_2 = \frac{P - E}{E} \times \frac{[H^+]^2}{K_1'} - [H^+]$$

$$= \frac{14.68}{0.138} \times \frac{(1.1 \times 10^{-14})^2}{1.05 \times 10^{-12}} - 1.10 \times 10^{-14}$$

$$= (1.22 - 1.10)10^{-14} = 1.2 \times 10^{-15}$$

TABLE I

PARTITION COEFFICIENT OF OSMIUM TETROXIDE BETWEEN WATER AND CARBON TETRACHLORIDE AT 25° (10 ml. CCl<sub>4</sub>, 20 ml. aqueous solution)

Ionic strength, $M$	Original concn. OsO <sub>4</sub> in aqueous phase, $M$	$P = \frac{[OsO_4]_{CCl_4}}{[OsO_4]_w} + \frac{[H_{2n-1}OsO_4^-]_w}{[H_{2n-2}OsO_4^{2-}]_w}$		Av.
		$\frac{[OsO_4]_{CCl_4}}{[OsO_4]_w}$	$\frac{[H_{2n-1}OsO_4^-]_w}{[H_{2n-2}OsO_4^{2-}]_w}$	
0.0	0.0024	13.12	13.12	13.0
		12.95	12.87	
1.0	.00081	14.72	14.62	14.7
		14.70	14.72	
1.0	.0016	14.65	14.91	14.9
		14.95	14.97	

TABLE II

EXTRACTION COEFFICIENT OF OSMIUM TETROXIDE BETWEEN SODIUM HYDROXIDE SOLUTION AND CARBON TETRACHLORIDE AND IONIZATION CONSTANTS OF PEROSMIC ACID (25°, 1.0  $M$  IONIC STRENGTH)

Original concn. OsO <sub>4</sub> in aqueous phase, $M$	$pH$	$E = \frac{[OsO_4]_{CCl_4}}{\Sigma [Os]_w}$		Av. <sup>a</sup>	$K_1' \times 10^{13}$	$K_2 \times 10^{15}$
		Range	Av. <sup>a</sup>			
0.00081	12.46	3.51 - 3.57	3.55	1.09	1.3 <sup>c</sup>	
.00081	12.77	1.94 - 1.98	1.95	1.11		
.00081	13.96 <sup>b</sup>	0.128 - 0.134	0.130	..		
.0016	12.47	3.77 - 3.94	3.85	0.98		
.0016	12.78	2.09 - 2.16	2.14	0.99		
.0016	13.96 <sup>b</sup>	0.144 - 0.148	0.146	..	1.4 <sup>d</sup>	

<sup>a</sup> Four determinations in each set. <sup>b</sup> Ionic strength somewhat greater than 1  $M$ . <sup>c</sup> Based on  $K_1' = 1.1 \times 10^{-12}$ . <sup>d</sup> Based on  $K_1' = 1.0 \times 10^{-12}$ .

The figures for  $\log I_0/I$  at 420  $m\mu$  for solutions of  $pH$  10.75-12.9 lead to the values  $\epsilon_1$  (molar extinction coefficient of primary perosmate ion) = 610 and  $K_1' = 1.02 \times 10^{-12}$ . These constants give close agreement between the measured and calculated extinction values in the range in which the secondary ionization of perosmic acid does not play a significant role

$pH$	10.75	11.90	12.60	12.91	13.54
$\log I_0/I$ obsd. ( $3.15 \times 10^{-4} M$ OsO <sub>4</sub> )	0.011	0.086	0.154	0.173	0.203
$\log I_0/I$ , calcd.	0.013	0.086	0.154	0.171	(0.188)

At  $pH$  13.54 the secondary ionization of perosmic acid becomes appreciable, and the calculated op-

tical density is lower than the observed density, inasmuch as  $\epsilon_2 > \epsilon_1$ .

Because of the small value of  $K_2$ , a very high hydroxyl ion concentration is required to convert most of the primary anion into the secondary anion. The high electrolyte concentration disturbs the normal absorption characteristics of the secondary anion. As may be seen from Fig. 1, a maximum value of the extinction coefficient at 360  $m\mu$  is found in about 7  $M$  potassium hydroxide; above this alkalinity the value slowly decreases. The maximum ( $\sim 2600$ ) is taken to be the approximate value of  $\epsilon_2$ . In 1:0  $M$  potassium hydroxide at 25-26°, the ratio of the concentrations of the two ions is

$$\frac{[H_{2n-2}OsO_4^{2-}]}{[H_{2n-1}OsO_4^-]} = \frac{1530 - 1270}{2600 - 1530} = 0.243$$

(The value of  $\epsilon_1$  as calculated from  $K_1'$ , the approximate value of  $K_2$ , and the extinction in 0.125  $M$  potassium hydroxide solution at unit ionic strength, is 1270; at this alkalinity 89% of the osmium is present as the primary anion, 2% as the secondary anion, and 9% as perosmic acid.)

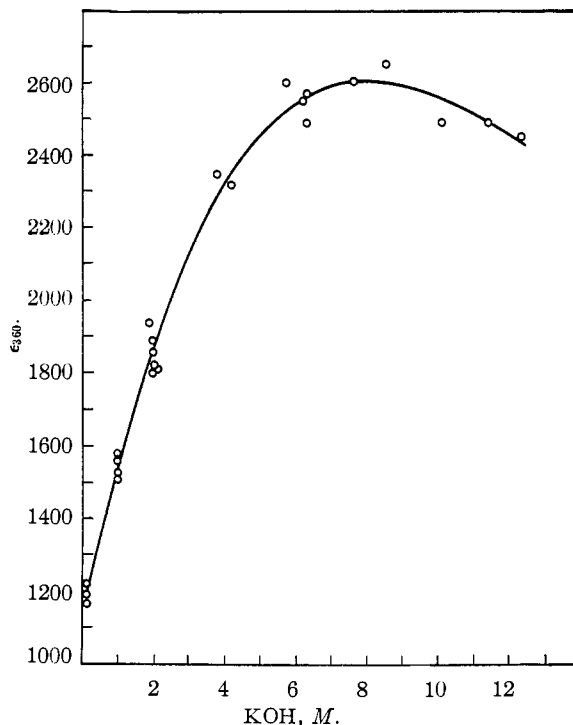


Fig. 1.—Apparent molar extinction coefficient of osmium tetroxide ( $3 \times 10^{-4} M$ ) at 360  $m\mu$  in potassium hydroxide solutions (25-26°).

The  $pH$  of 1.0  $M$  potassium hydroxide as measured with a glass electrode is 13.90. The mixed constant  $K_2$ , based on hydrogen ion activity, is then equal to  $0.243 \times 1.25 \times 10^{-14} = 3 \times 10^{-15}$ .

**Discussion**

The present value of 13.0 for  $P$  at virtually zero ionic strength agrees well with the earlier average 12.3 found by Yost and White.<sup>2</sup> The increase in  $P$  to 14.8 at 1.0  $M$  ionic strength is in accord with the salting-out effect of electrolytes on osmium tetroxide. The present value of  $1.0 \times 10^{-12}$  for  $K_1'$  at 1.0  $M$  ionic strength is comparable with Yost and

White's value  $8 \times 10^{-13}$  at 0.06 *M* ionic strength (and based on  $[H^+]$  instead of  $a_{H^+}$ ).

The partition and spectrophotometric methods agree in indicating a value a little greater than  $1 \times 10^{-15}$  for  $K_2$  of perosmic acid at 1.0 *M* ionic strength. Greater weight should be given the spectrophotometric value ( $3 \times 10^{-15}$ ) than the partition value ( $1.4 \times 10^{-15}$ ), so that instead of averaging the two figures, we shall accept  $3 \times 10^{-15}$  as the value of  $K_2$ .

If one assumes the applicability of the general rule that successive ionization constants of an oxy-

gen acid differ by the factor  $\sim 10^{-5}$ , the primary ionization constant of perosmic acid should be about  $10^{-10}$ . Since the apparent constant based on total osmium in solution is  $10^{-12}$ , some support is thus obtained for the belief that a large fraction of the osmium tetroxide exists as such in solution. It may also be noted that the value  $10^{-10}$  for  $K_1$ , the true ionization constant, agrees with  $K_1$  for acids of the type  $X(OH)_n$ , most of which have primary ionization constants of  $10^{-9}$  to  $10^{-11}$ .

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## Lead Citrates, Complexes and Salts, their Composition, Structure and Behavior

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The composition and structure of the complexes and salts of lead citrate were studied at low and high *pH*'s. The phenomena observed may be accounted for as follows. A soluble complex of the composition  $[PbCi_2]^{4-}$  is obtained quantitatively from the components at *pH*  $\sim 7.0$ . The latter gives on addition of lead an insoluble salt of the composition  $Pb_2Ci_2$  or  $Pb_3[PbCi_2]$ , which redissolves at *pH*  $\leq 3.0$ . At high *pH*'s (*pH*  $\geq 9.5$ ) the anion complex  $[PbCi']^{2-}$  is formed quantitatively. Between *pH* 7–9.5 the complexes  $[PbCi_2]^{4-}$  and  $[PbCi']^{2-}$  are obtained side by side in solution. At *pH*  $\sim 8.0$   $[PbCi']^{2-}$  forms, on the addition of lead, the insoluble salt  $Pb[PbCi'] \cdot [PbCi']^{2-}$  may be presented as an anion of an acid  $[PbCi]^{1-}$  for which *pk* = 7.5. Under different experimental conditions two insoluble salts of different structures but of the same empirical composition  $Pb_2Ci_2$ , may exist.

The investigation of lead citrate is a continuation of the studies of metal complexes with citrate or tartrate.<sup>1</sup> The study of lead citrate may be of special interest because of its role in physiology and the therapy of lead poisoning, where lead is removed by complex formation with citrate.<sup>2</sup>

### Experimental Details

**Reagents and Solutions.**—Stock solutions of lead nitrate and sodium citrate were prepared by weighing the salts  $Pb(NO_3)_2$  and  $Na_3C_6H_5O_7 \cdot 2H_2O$  (both C.P. Baker Analyzed), and solutions of the required concentration were then prepared by dilution with distilled water.

**Apparatus and Procedure. Heterometer.**—A "Heterometer" designed and constructed by the first author specially for electrophotometric titrations involving suspensions was used. The light passed vertically during the titration through the cylindrical absorption cell (diameter = 5.2 cm.) and fell on the photoelectric cell. The readings on the galvanometer were made with an accuracy of  $\pm 0.001$  microamp., and the optical density ( $D = \log I_0/I$ ) was calculated to three decimal places. The readings were recorded at 0.1–0.2 cc. intervals only after a constant value was obtained, usually after a few seconds to a minute. The usual rate of stirring of the solution was 600 r.p.m. and was generally the maximum consistent with stable measurements. Experiments were repeated after several months to check the reproducibility of the density curves, which, in general, was very good. The maximum optical density values varied somewhat, but the critical points on the horizontal axis remained the same in all cases.

**Heterometry**<sup>3</sup> deals with the photometric study of chemical reactions in suspensions on a quantitative basis. It is concerned with reactions which occur in the solution as well

as in the solid state. *Heterometric titration curves* (optical density curves) are obtained and the *critical points* determined. From each heterometric curve at least two or three critical points may be derived. They are: the point of the "initial precipitation," the "maximum density" point and the point of "complete dissolution." In most cases additional critical points are obtained.

Since heterometry deals primarily with end-points it does not matter whether the particles are of unit or varying size.

Many thousands of heterometric curves were obtained by the author with co-workers in the past four years. We were convinced by the results that heterometry is especially suitable for the study of soluble and insoluble complex compounds and for the heterometric microdetermination of metals or other compounds.

***pH* Measurements.**—A Beckman Model H2 *pH* meter in conjunction with a "Beckman Glass electrode" and a "Beckman saturated calomel electrode" was used for all *pH* titrations. Readings were taken at 0.1–0.2 cc. intervals after each addition of titrating solution and with continuous stirring. The time required for the reading to become constant varied with the reactions studied, especially when redissolving occurred, but in no case was a *pH* value recorded until the reading became constant.

**Conductivity Measurements.**—A "Serfass Conductivity Bridge Model R.C.M. 15," manufactured by Industrial Instruments, Inc., U.S.A., was used for the conductometric experiments. The conductance cell has been described in a previous paper.<sup>4</sup> The heterometric and *pH* titrations were carried out at room temperature (18–27°).

### Results and Discussion

This study of lead citrate was made by physical methods only. No claim is made that the problem presented is in any way exhausted. The reactions occurring at different *pH*'s are much too complicated for a detailed analysis. Nevertheless, an attempt was made by us to present formulas for the compounds obtained which conform with the experimental results. Here, as in many other reactions studied by us, we assume that the hydrogen of the hydroxy group of citrate is quantitatively released at high *pH* and replaced by the cation.

(4) M. Bobtelsky and A. E. Simchen, *THIS JOURNAL*, **64**, 445 (1942).

(1) M. Bobtelsky and A. E. Simchen, *THIS JOURNAL*, **64**, 2592 (1942); *Compt. rend.*, **208**, 1646 (1939); *Bull. soc. chim.*, **17**, 870 (1950); M. Bobtelsky and J. Jordan, *THIS JOURNAL*, **67**, 1824 (1945); **69**, 2286 (1947); M. Bobtelsky and C. Heitner, *Bull. soc. chim.*, **18**, 494 (1951); **19**, 358 (1952).

(2) S. S. Kety and T. V. Letonoff, *C. A.*, **35**, 37149 (1941); **36**, 2028<sup>2</sup> (1942); **37**, 2460<sup>3</sup> (1943); F. Auerbach and H. Weber, *Z. anorg. Chem.*, **147**, 68 (1925).

(3) M. Bobtelsky and Bar-Gadda, (a) *Bull. soc. chim. France*, 278 (1953); (b) *Ann. Chim. Acta*, 1953; M. Bobtelsky and B. Graus, (a) *Bull. Research Council of Israel*, 1953; (b) *Ann. Chim. Acta*, 1953.