[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Reactions of Divalent Palladium with Ethylenediaminetetraacetic Acid

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Ethylenediaminetetraacetic acid has been shown to complex with divalent palladium. In the *p*H range 3.82–8.95 the formula of the complex is $PdY^=$. The logarithm of its stability constant is 18.5 ± 0.6. Photometric, complexometric, potentiometric and chemical evidence support these conclusions.

Ethylenediaminetetraacetic acid has been found to complex strongly with divalent palladium. The existence of this complex and its composition is supported by spectrophotometric, potentiometric, complexometric and chemical evidence.

This study was purposely begun with chloride solution because palladium is usually available as the chloride and solutions are frequently made from this salt. Divalent palladium complexes so strongly with ethylenediaminetetraacetic acid (hereafter called EDTA) that no evidence of competition by the chloride complex could be detected.

The use of the color complex between EDTA and divalent palladium for the spectrophotometric determination of palladium has been reported.[1] The present paper reports a detailed study of the nature of the complex, the ratio of metal to EDTA, the charge on the complex, the probable formula and an evaluation of the stability constant.

Reagents. Palladous Chloride Solution.—One gram of Coleman and Bell Reagent palladous chloride was dissolved in 1 liter of 0.1 *M* hydrochloric acid. Solution was not immediate but required an hour of standing. The presence of $PdCl_4^=$ was verified spectrophotometrically by comparison with data of Cohen and Davidson.[2] The exact strength of the solution was established analytically by precipitation with dimethylglyoxime according to the modified plan of Gilchrist and Wichers.[3] The palladium chloride was also examined spectrographically and only slight traces of platinum were found.

Chloride-free Palladous Perchlorate Solution.—A solution of palladous perchlorate was prepared according to the method of Templeton, Watt and Garner.[4] A portion of the palladous chloride solution was made slightly basic with potassium hydroxide. The resulting precipitate of palladous hydroxide was washed with water on a sintered glass funnel until chloride free. It was then dissolved in concentrated perchloric acid and diluted with water to a known volume. The concentration of palladium was determined by precipitation of the palladium in an aliquot with dimethylglyoxime.

Ethylenediaminetetraacetic Acid.—Analytical reagent grade disodium salt was obtained from the F. W. Bersworth Co. The free acid, also obtained from F. W. Bersworth Co., was recrystallized twice from distilled water and was used in the determination of the stability constant.

Apparatus.—Absorption spectra were measured with a Beckman DU spectrophotometer, equipped with tungsten and hydrogen sources and 1 cm. silica cells.

Potential measurements were made at 25 ± 0.1° with a Leeds and Northrup Type K potentiometer and standard Eppley cell. *p*H measurements were made with a Beckman Model G battery operated meter.

The ionic charge on the palladium-EDTA complex was determined with a three compartment cell similar to that described by Duval.[5] The power supply included a transformer, d.c. outlet, 0–500 volt voltmeter and a milliammeter. The potential could be regulated to supply constant current.

Double distilled water was used throughout the work and glassware and weights were calibrated by conventional methods.

Spectrophotometric Study of Divalent Palladium-EDTA Complex.—A marked change in the absorbance of divalent palladium chloride solution occurs upon addition of EDTA. Figure 1 shows absorbance curves for solutions made from palladous chloride solution containing 115 p.p.m. of palladium. Curve 1 shows the absorbance of a solution containing palladium and EDTA in neutral solution. Curves 2 and 5 show the effect of EDTA on the absorbance in a solution of *p*H 1.6. Curves 3 and 4 similarly show the effect of EDTA at *p*H 13.0.

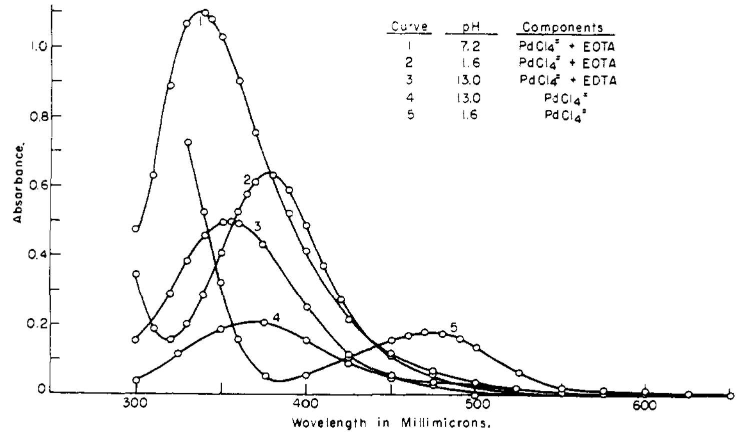

Fig. 1.—Absorbance curves for palladous chloride–EDTA solutions.

Observation of the wave length of maximum absorbance as a function of *p*H indicates, as shown in Fig. 2, that the wave length of maximum absorbance is dependent upon the *p*H of the solution but that there are three *p*H regions 1.6–2.0, 4.5–9.5 and 11.5–13.5 where the wave length of maximum absorbance is independent of *p*H. Figure 2 is based on absorbance curves published earlier.[2] These data indicate the probability of at least three different species in these respective *p*H ranges.

The ratio of EDTA to palladium in the complex was determined by the method of continuous variations.[6] The results, shown in Fig. 3, indicate that a ratio of EDTA to palladium of 1:1 exists. This suggests that the variation in the complex with *p*H, as indicated by change in absorbance, may be caused by the addition of one or more protons or hydroxyl ions to the EDTA-palladium complex since there is no change in the ratio of EDTA to palladium. In the experiments represented in Fig. 3, *x* volumes of 0.00054 *M* palladous chloride were varied with 1 − *x* volumes of 0.00054 *M* EDTA-disodium salt. *y* is the *increase in absorbance* due to formation of a palladium-EDTA complex.

A 1:1 ratio for EDTA to palladium has also been shown by a study of the complexometric titration of palladium with EDTA.[7]

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[1] W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **26**, 1768 (1954).

[2] A. J. Cohen and J. Davidson, THIS JOURNAL, **73**, 1955 (1951).

[3] R. Gilchrist and E. Wichers, *ibid.*, **57**, 2565 (1935).

[4] D. H. Templeton, G. H. Watt and C. S. Garner, *ibid.*, **65**, 1608 (1943).

[5] C. Duval, *Compt. rend.*, **200**, 2175 (1935).

[6] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[7] W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **27**, 535 (1955).

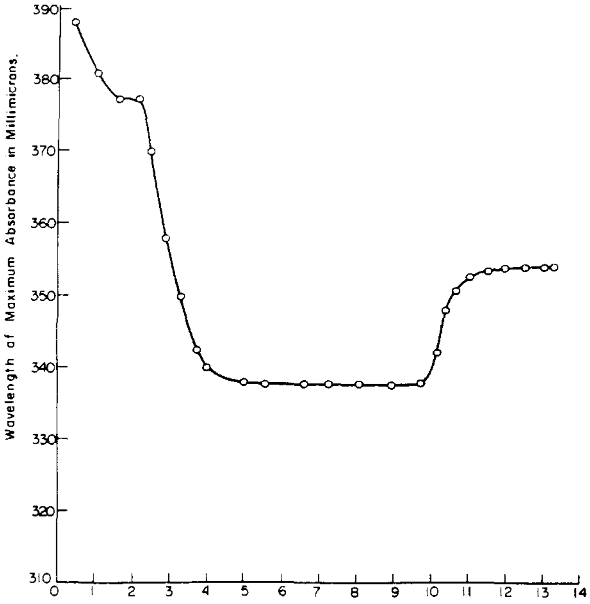

Fig. 2.—Effect of pH on wave length of maximum absorbance.

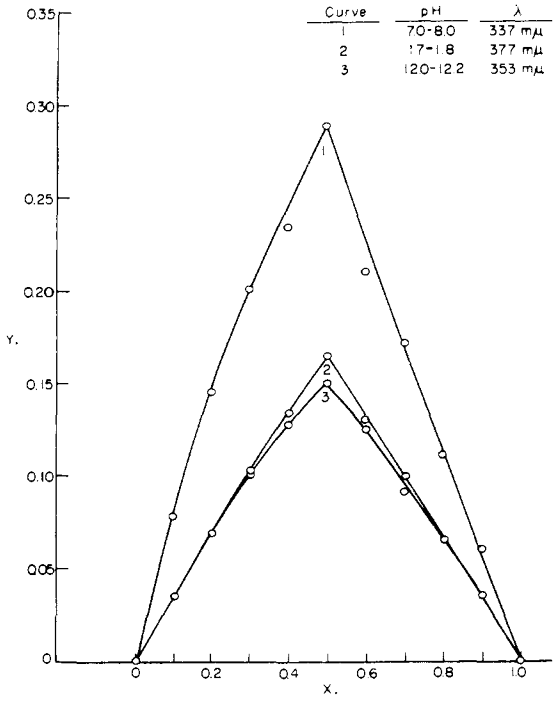

Fig. 3.—Ratio of palladium (x) to EDTA ($1 - x$) in complex.

Further information on the nature of the complex was obtained by studying the movement of species between charged electrodes. Solutions containing palladium-EDTA mixtures were placed in the three compartment cell shown in Fig. 4. The center compartment has a volume of 40 ml. while the anode and cathode compartments each hold 50 ml. Platinum electrodes were placed in the anode and cathode compartments and d.c. voltages up to 1000 volts were available. The anode and cathode compartments were each filled with 0.1 M potassium chloride. The migration of the palladium depended strongly upon the pH of the solution. At a pH of 1.8 and an applied voltage of 400 volts and 20 milliamp current, only a trace of palladium was found in the anode compartment after 1 hour. At a pH of 2.5, a small amount appeared at the anode. At pH 10 about ten times as much palladium appeared in the anode compartment.

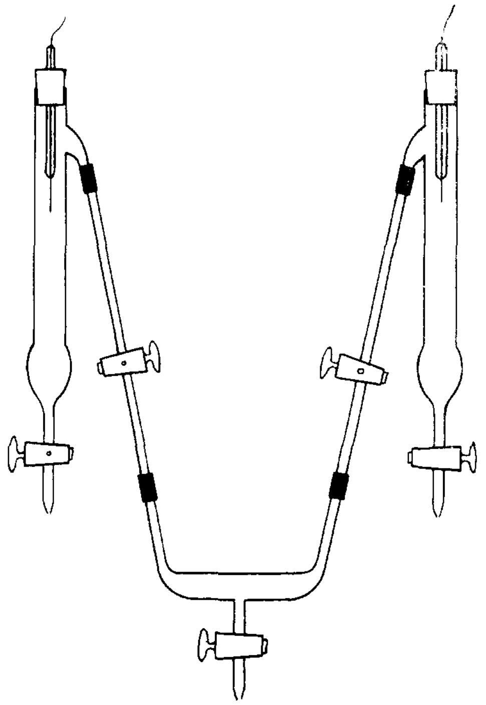

Fig. 4.—Apparatus for ion migration.

The four acid dissociation constants for EDTA are given by Schwarzenbach and Ackermann[8] as $10^{-2.00}$, $10^{-2.67}$, $10^{-6.16}$ and $10^{-10.26}$ at $u = 0.1$ and 20°. The effect of pH upon migration may be interpreted in view of these constants. At a pH of 1.8, the dominant form is H_2PdY where Y represents EDTA. Small amounts of $HPdY^-$ also exist which accounts for the slight migration to the anode at this low pH. At a pH of 2.5, the concentration of $HPdY^-$ is greater, thus accounting for more migration in this pH range.

In neutral or basic solution, $PdY^=$ or $PdOHY^≡$ is dominant. Goffart, Michel and Duyckaerts[9] report similar complexes of mercury and EDTA, $HHgY^-$, $HgY^=$ and $Hg(OH)Y^≡$ in slightly acid, neutral and basic solutions, respectively. Schwarzenbach and Ackermann[8] also report the formation of $HCaY^-$, $CaY^=$ and $Ca(OH)Y^≡$ in acid, neutral and basic solutions.

It may now be concluded that divalent palladium forms complexes with EDTA whose formulas are H_2PdY (strongly acid), $HPdY^-$ (slightly acid), $PdY^=$ (neutral) and $PdOHY^≡$ (basic) and that these complexes are stronger than the corresponding chloride complexes.

Determination of Stability Constant for $PdY^=$.—In the pH range 3.7-9.0 the species $PdY^=$ formed by the reaction $Pd^{++} + Y^{≡≡} = PdY^=$ is dominant. The report of a reversible palladium-palladous ion electrode by Templeton, Watt and Garner[4] makes possible the measurement of the Pd^{++} ion in EdTA solutions and thus the evaluation of the stability constant, $K = [PdY^=]/([Pd^{++}][Y^{≡≡}])$, by the method of Bjerrum and Nielsen.[10] In the following calculation of stability constants, $[PdY^=]$ is assumed equal to the original concentration of palladium since a large excess of EDTA is present and the stablity of the $PdY^=$ complex is so great. The quantity $[Pd^{++}]$ is measured potentiometrically and $[Y^{≡≡}]$ is calculated from the total concentration of EDTA present (C_s) and the pH of the solution. This calculation follows.

Schwarzenbach and Ackermann[8] have determined the four

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(8) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

(9) J. Goffart, G. Michel and G. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(10) J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

acid dissociation constant for EDTA for $u = 0.1$ and $T = 20°$.

$$K_1 = \frac{[\mathrm{H_3Y^-}][\mathrm{H^+}]}{[\mathrm{H_4Y}]} = 10^{-2.00}$$

$$K_2 = \frac{[\mathrm{H_2Y^{=}}][\mathrm{H^+}]}{[\mathrm{H_3Y^-}]} = 10^{-2.67}$$

$$K_3 = \frac{[\mathrm{HY^{\equiv}}][\mathrm{H^+}]}{[\mathrm{H_2Y^-}]} = 10^{-6.16}$$

$$K_4 = \frac{[\mathrm{Y^{==}}][\mathrm{H^+}]}{[\mathrm{HY^{\equiv}}]} = 10^{-10.26}$$

For 25° and $u = 0.2$, these constants become $K_1 = 10^{-1.95}$, $K_2 = 10^{-2.62}$, $K_3 = 10^{-6.00}$ and $K_4 = 10^{-10.08}$, values used in the calculation of the stability constant. If the amount of EDTA is much greater than the concentration of palladium, then $C_s = [\mathrm{Y^{==}}] + [\mathrm{HY^{\equiv}}] + [\mathrm{H_2Y^-}] + [\mathrm{H_3Y^-}] + [\mathrm{H_4Y}]$. When substitution is made for each term from the expression for K_1, K_2, K_3 and K_4, $[\mathrm{Y^{==}}]$ becomes

$$[\mathrm{Y^{==}}] = \frac{C_sK_1K_2K_3K_4}{K_1K_2K_3K_4 + K_1K_2K_3\,[\mathrm{H^+}] + K_1K_2[\mathrm{H^+}]^2 + K_1[\mathrm{H^+}]^3 + [\mathrm{H^+}]^4}$$

$[\mathrm{Y^{==}}]$ can then be calculated at any *p*H since C_s, K_1, K_2, K_3 and K_4 are known.

Assuming the validity of the Nernst expression for the reversible palladium–palladous ion electrode

$$E = E^0 - \frac{0.0591}{2}\log\,[\mathrm{Pd^{++}}]$$

and substituting for $\mathrm{Pd^{++}}$ from the expression for the equilibrium constant sought, $K = \frac{[\mathrm{PdY^{=}}]}{[\mathrm{Pd^{++}}][\mathrm{Y^{==}}]}$, the equation for the potential of the palladium electrode becomes

$$E = E^0 - \frac{0.0591}{2}\log\,[\mathrm{PdY^{=}}] + \frac{0.0591}{2}\log[\mathrm{Y^{==}}] + \frac{0.0591}{2}\log K$$

If values of E are measured for corresponding solutions containing EDTA, then this equation may be solved for K. The $E°$ value, −0.936 volt, used was determined by measurements of the potential of the Pd–$\mathrm{Pd^{++}}$ electrode in perchlorate solutions of ionic strength 0.2 at a temperature of 25°.

Measurements of the potential of the palladium electrode have been made with the electrode described by Templeton, Watt and Garner.[4] It consists of a palladized platinum wire surrounded by spongy palladium. Spongy palladium was prepared by electrolysis of a palladous chloride–hydrochloric acid solution. The metal was washed repeatedly with water, dried at room temperature and then heated in a vacuum for 30 minutes to remove occluded water and hydrogen. Equilibrium was reached only slowly with this electrode. Preliminary vigorous agitation of the spongy palladium for 10 minutes with the solution to be measured brought rapid equilibrium. A special 25-ml. beaker with quarter-inch bubble blown in its base was used for making potential measurements. After the spongy palladium and solution were transferred to the beaker, the beaker was given a swirling motion which caused the spongy palladium to collect in the depression. The palladized platinum wire was immersed in the pool of spongy palladium and its potential measured against a saturated calomel electrode.

Ten determinations of the equilibrium potential of the palladium–palladous electrode in palladium–EDTA solution have been made over the *p*H range 3.72–8.95. The results are shown in Table I.

All solutions were 0.0192 *M* in EDTA and 0.00037 *M* in palladium perchlorate. The ionic strength was adjusted to 0.2 with perchloric acid and the *p*H was adjusted with dilute potassium hydroxide. Table I also shows the calculated values of log *K*, the stability constant for the $\mathrm{PdY^{=}}$ complex. The mean value $10^{18.5 \pm 0.6}$, agrees well with that predicted by the theory of Mellor and Maley[11] who estimate that the EDTA complex of palladium should be slightly more stable than that for copper ($K = 10^{18.4}$). The small but definite break in the trend of values in the middle *p*H range cannot be accounted for.

TABLE I

POTENTIOMETRIC DETERMINATION OF THE STABILITY CONSTANT FOR THE $\mathrm{PdY^{=}}$ COMPLEX

*p*H	$E_{\text{obs.}}$ *vs.* S.C.E.	Log *K*	*p*H	$E_{\text{obs.}}$ *vs.* S.C.E.	Log *K*
3.72	−0.3306	19.1	5.64	−0.2456	18.3
3.82	− .3263	19.1	6.00	− .2392	17.9
3.89	− .3305	18.8	6.21	− .2280	18.0
4.57	− .2886	18.8	7.35	− .1874	18.1
5.48	− .2632	18.0	8.95	− .1295	18.4
				Mean	18.5 ± 0.6

Summary

1. Palladium forms complexes with EDTA which are sensitive to *p*H.
2. The ratio of palladium to EDTA is shown by spectrophotometric and complexometric data to be 1:1 in the *p*H range 1.6–13.0.
3. It is concluded that in the *p*H range 3.72–8.95 the complex has the formula $\mathrm{PdY^{=}}$.
4. The stability constant has been calculated from experimental data and found to be $10^{18.5 \pm 0.6}$ at $u = 0.2$ and 25°.

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[11] P. D. Mellor and L. Maley, *Nature*, **159**, 370 (1947); **161**, 436 (1948).