in size of the central atom or to radical differences in the reaction mechanism. The first possibility can be better evaluated only when more data are available on additional members of the tetra-alkyl groups. As for the second alternative, a more thorough examination of the decomposition of tetraethyl lead would undoubtedly yield valuable information concerning its mechanism and energy of activation.

Summary

The thermal decomposition of tetramethyltin has been investigated between 440 and 493° over a range between 5 and 185 mm. initial pressure.

By the criteria of half-life periods, times for a given fractional pressure increase and initial rates, the reaction was found to be predominantly of the first order above 80 mm. initial pressure. At lower initial pressures the order increases, approaching that of second.

The specific velocity constant of the primary process was found to be $k_0 = 8.32 \times 10^{21} e^{-82,400/RT}$. Rate constants calculated by an indirect method agreed well with those obtained directly.

The reaction was found to be homogeneous once the reaction vessel was thoroughly coated with a deposit of tin and carbon.

Nitric oxide produced no inhibition but instead caused a slight catalytic acceleration of the primary process.

Chemical analyses made over the entire range of decomposition revealed the predominant gaseous product to be methane, together with some hydrogen and ethylene. Tin and carbon were also found as a deposit on the walls.

Based upon the kinetic data and the chemical analyses, a probable reaction mechanism was proposed.

An explanation is offered for the changes in activation energy observed in going from the methyl to ethyl to propyl tetra-alkyls thus far investigated.

BROOKLYN, N. Y. RECEIVED JANUARY 18, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

The Polarographic Reduction of the Platinum Metals

BY J. B. WILLIS

In a previous communication[1] the polarographic reduction of rhodium compounds was discussed in detail. In the present paper similar work is extended to the other platinum metals. With the exception of a recent paper on the polarographic reduction of osmium tetroxide,[2] the only published work in this field seems to be that dealing with catalytic hydrogen waves produced in acid solutions containing small amounts of the platinum metal chlorides.[3,4]

Theory

It was shown in the previous paper[1] that although rhodium trichloride itself was rapidly decomposed by mercury, complex salts of rhodium could be obtained which were stable toward mercury, and which were reducible at the dropping electrode. In the present work it is shown that the other platinum metals also form stable complexes, which in some cases give polarographic steps.

In order to calculate n, the number of electrons involved in each reduction step, the Ilkovič equation was applied and the log plot calculated in the previously described way. As explained before, in the calculation of the diffusion coefficient of a complex metal ion conductivity data for similar ions of other metals can be used without any serious error.

Experimental

A manual instrument was used, similar to the previously described one. All measurements were carried out at 25°, air being displaced from the solutions by purified nitrogen. The half-wave potentials $(E_{1/2})$ are expressed relative to the saturated calomel electrode, and are considered to be in error by not more than ±10 mv.

The solutions used were prepared by adding 1 ml. of an analyzed stock solution of a salt of the metal to an excess of the complex-forming substance, which also acted as supporting electrolyte, warming to complete the reaction, and making up to 50 ml. The solutions were 0.001 M with regard to the metal to be studied, unless otherwise stated.

Results

Chloro-complexes of the Platinum Metals.—All the chlorosalts used as stock solutions in this work were spontaneously decomposed by mercury, though in the case of the hexachlororuthenate and aquopentachlororuthenate the decomposition was very slow. No polarographic steps could be obtained from any of the chlorosalts. With the exception of di-ethylenediamine platinous chloride, however, none of the complexes studied polarographically were decomposed even by long standing over mercury.

Ruthenium.—Potassium hexachlororuthenate $K_2[RuCl_6]$ was used for Ru^{IV}, and potassium

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[1] Willis, THIS JOURNAL, **66**, 1067 (1944).

[2] Crowell, Heyrovsky, and Engelkemeir, *ibid.*, **63**, 2888 (1941).

[3] Herasymenko and Slendyk, *Coll. Czech. Chem. Comm.*, **5**, 479 (1933).

[4] Herasymenko and Slendyk, *Z. physik. Chem.*, **162**, 223 (1932).

aquopentachlororuthenate $K_2[RuCl_5H_2O]$ for Ru^{III}. No steps could be obtained, however, either from Ru^{IV} or Ru^{III} in *M* potassium cyanide, *M* potassium thiocyanate, *M* ammonia–*M* ammonium chloride, or *M* pyridine–*M* potassium chloride. In each case the distinct change of color taking place on warming the ruthenium salt with the supporting electrolyte indicated that coördination had taken place to some extent at least.

Osmium.—The only compound studied was potassium osmocyanide $K_4[Os(CN)_6]$, which was prepared by the method of Krauss and Schräder,[5] and isolated in the solid state. It gave no polarographic step either in *M* potassium cyanide or in *N* potassium sulfate.

Iridium.—Ammonium hexachloroiridate and ammonium hexachloroiridite were used for Ir^{IV} and Ir^{III}, respectively. Coördination took place but no steps were obtained, in *M* potassium cyanide, *M* ammonium hydroxide–*M* ammonium chloride, *M* potassium thiocyanate (neutral), *M* ethylenediamine–*M* potassium chloride, *M* pyridine–*M* potassium chloride.

Platinum.—Potassium chloroplatinite was used as stock solution for Pt^{II}. Although immediate coördination took place, no steps were obtained in the following electrolytes: *M* potassium cyanide, *M* ammonia–*M* ammonium chloride, *M* pyridine–*M* potassium chloride, *M* ethylenediamine–*M* potassium chloride. In the last-named solution platinum was deposited slowly on the mercury, showing decomposition to take place. The compounds formed in these solutions are presumably quite analogous to those formed by Pd^{II} (see below).

Palladium

Palladous chloride, mixed with an equivalent amount of sodium chloride, was used as a stock solution for Pd^{II}.

Cyanide Media.—The stock solution was immediately decolorized by *M* potassium cyanide and a step was obtained at −1.77 v., just before the decomposition of the supporting electrolyte, so that the height could not be measured with the highest accuracy. The dropping of the mercury electrode at the top of the step was somewhat irregular. The height of the step was proportional to the concentration over the range studied, *viz.*, 2×10^{-4} *M* to 5×10^{-3} *M*. The log plot was a straight line of reciprocal slope 0.034 v.

Attempts were made to separate the palladium step from that of the potassium by reducing the concentration of the potassium cyanide which usually has the effect of shifting $E_{1/2}$ of complexes to a less negative value. However, no step was found either in 0.1 *M* or in 0.025 *M* potassium cyanide, but in 0.1 *M* potassium cyanide–*M* potassium chloride the step appeared at −1.757 v. This phenomenon of the step disappearing with dilution of the supporting electrolyte seems to depend on the total activity of the ions of the supporting electrolyte and not merely on that of the complex-forming ion.

The ion present in these cyanide solutions is certainly $[Pd(CN)_4]^{--}$. On extrapolating to infinite dilution the conductivity values of Walden[6] for sodium platinocyanide and applying the Ilkovič equation, *n* was found to be 2.0 electrons, a conclusion borne out by the slope of the log plot, *viz.*, 0.034 v., which indicates a reversible two-electron reduction. Thus the electrode process appears to be

$$[Pd(CN)_4]^{--} + 2e = Pd + 4CN^-$$

Ammoniacal Solutions.—The stock solution on addition of *M* ammonia–*M* ammonium chloride gave a cream-colored precipitate of dichlorodiammine palladium which dissolved in excess of the ammoniacal solution to give presumably the tetrammine palladous chloride. A well-defined step was obtained, whose half-wave potential was not independent of the concentration of palladium. $E_{1/2}$ was −0.797 v. in 5×10^{-3} *M*, −0.734 v. in 1×10^{-3} *M*, −0.719 v., in 2×10^{-4} *M* solutions. In the 5×10^{-3} *M* solution a maximum occurred which was suppressed by 0.005% methyl red. The log plot was a straight line of reciprocal slope 0.049 v., which indicates an incompletely reversible reduction. The step-height was proportional to the concentration over the above range. Application of the Ilkovič equation, using the conductivity data of Lorenz and Posen[7] for the tetrammine platinous ion, gave *n* = 2.0 electrons. The electrode process thus seems to be

$$[Pd(NH_3)_4]^{++} + 2e = Pd + 4NH_3$$

Pyridine Medium.—The addition of *M* pyridine–*M* potassium chloride to the stock palladium solution produced a cream-colored precipitate of dichlorodipyridine palladium, soluble in an excess of the supporting electrolyte to give the tetrapyridine salt $[Pd\ py_4]Cl_2$. This salt is stable in solution in the presence of excess pyridine.[8]

A step was found at a potential which varied somewhat with the concentration: $E_{1/2}$ was −0.361 v. in 5×10^{-3} *M* −0.321 v. in 1×10^{-3} *M*, and −0.313 v. in 2×10^{-4} *M* solution. The log plot was a straight line with a reciprocal slope of 0.030 v., which indicates a reversible two-electron reduction. The height of the step was proportional to the concentration over the above range, and application of the Ilkovič equation, using the conductivity data[7] for tetrapyridine platinous ion gave *n* 1.75. The reason for this rather low value is not apparent. Here again reduction to metal occurs in one step.

Ethylenediamine.—In *M* ethylenediamine–*M* potassium chloride a step was obtained at about

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(5) Krauss and Schräder, *J. prakt. Chem.*, **119**, 279 (1928).

(6) Walden, *Z. physik. Chem.*, **2**, 74 (1887).

(7) Lorenz and Posen, *Z. anorg. allgem. Chem.*, **96**, 81 (1916).

(8) Drew, Pinkard, Preston and Wardlaw, *J. Chem. Soc.*, 1895 (1932).

-0.76 v., but the top of the step was somewhat obscured by irregular dropping of the mercury electrode. In 0.1 M ethylenediamine–M potassium chloride a well-defined step was obtained in the presence of 0.005% methyl red; $E_{1/2}$ was -0.650 v. in 1×10^{-3} M, -0.628 v. in 2×10^{-4} M solution. In 5×10^{-3} M solution the dropping was very irregular and no measurements could be made. The log plot was a straight line of reciprocal slope 0.041 v., which suggests an incompletely reversible step. Using conductivity data[7] for $[\mathrm{Pt\ en_2}]\mathrm{Cl_2}$ n was found to be 2.0 electrons, showing the usual electrode reaction to take place

$$[\mathrm{Pd\ en_2}]^{++} + 2e = \mathrm{Pd} + 2\mathrm{en}$$

The Stability of Palladous-ammine Complexes.—From the foregoing results it is seen that palladous chloride coördinates with a number of amines to form complexes which are reduced to the metal at the dropping mercury electrode. In Table I a list of $E_{1/2}$ values is given for (1) solutions 0.001 M in palladium, M in amine, and M in potassium chloride, (2) solutions 0.001 M in palladium, 0.1 M in the amine, and M in potassium chloride. The slope of the log plot is also given as an indication of the reversibility of the reduction.

TABLE I

Amine	pK	$E_{1/2}$ (1), v.	$E_{1/2}$ (2), v.	Log plot
Pyridine	5.4	-0.320	-0.212	Straight line, 0.030 v.
Ammonia	9.3	$-$ .706	$-$ .700	Straight line, .049 v.
Monoethanolamine	9.4	$-$ .752	$-$ .637	.051 v.
Ethylenediamine	9.9	$-$ .76^a	$-$ .650^b	Not a straight line
Diethylamine	11.0	-1.22^a	$-$ .735	

^{a} Curve irregular in shape. ^{b} Maximum suppressed by 0.01% methyl red.

Two facts are apparent from this table: (a) The half-wave potential of the complex is the more negative, the more basic the amine, *i. e.*, the stability of the complex increases with the basic strength of the coördinating amine. This is in accord with chemical experience[9] in the case of palladium, though the reverse is true with most other metals.[10] (b) As the stability of the complex increases the reduction becomes less reversible. This may be due to the greater energy required to disrupt the complex ion, so that an overvoltage is required for its polarographic reduction.

Discussion

Although it is known that the complexes of $\mathrm{Pt^{II}}$ are in general more stable than their $\mathrm{Pd^{II}}$ analogs, it is surprising that their polarographic behavior is so widely different. None of the $\mathrm{Pt^{II}}$ complexes examined has been found to give a step, even in the case of $[\mathrm{Pt\ py_4}]^{++}$ which by the above argument would be expected to be less stable than most of the others. Whether the failure to give polarographic steps is really due to the high stability alone or whether there is some other factor involved, is an open question.

Some observations may be made on the cyanide complexes of Group VIII. The following complex cyanides are known to be stable in the solid state:

$\mathrm{Fe^{II}}$	$\mathrm{Fe^{III}}$	$\mathrm{Co^{III}}$	$\mathrm{Ni^{II}}$
$\mathrm{Ru^{II}}$		$\mathrm{Rh^{III}}$	$\mathrm{Pd^{II}}$
$\mathrm{Os^{II}}$		$\mathrm{Ir^{III}}$	$\mathrm{Pt^{II}}$

Their stability increases on passing down the column. Polarographic reduction of the trivalent complexes is possible to the divalent state only. In the center column the increase of stability from cobalt to iridium is shown by the increase in negativity of $E_{1/2}$ which indicates more difficult reduction. $E_{1/2}$ in M potassium cyanide[1] is -1.38 v. for $\mathrm{Co^{III}}$, -1.47 v. for $\mathrm{Rh^{III}}$, while $\mathrm{Ir^{III}}$ is not reducible polarographically under the same conditions. With the increase of stability of the trivalent state toward reduction, a corresponding instability of the divalent complexes toward water is to be expected, owing to the fact that the classical oxidation–reduction potential of the system $[\mathrm{M(CN)_6}]^{---} \rightarrow [\mathrm{M(CN)_6}]^{--}$ becomes greater than the standard potential of the process $2\mathrm{H_2O} + 2e = \mathrm{H_2} + 2\mathrm{OH^-}$. Hence the isolation of rhodo- and irido-cyanides will in all probability not be possible.

In the third column the $E_{1/2}$ values vary in the same way. $E_{1/2}$ is -1.38 v. for $\mathrm{Ni^{II}}$ and -1.77 v., for $\mathrm{Pd^{II}}$ in M potassium cyanide, while $\mathrm{Pt^{II}}$ is not polarographically reducible in this medium. It is remarkable that whereas the simple ionic reduction process $[\mathrm{Co(CN)_6}]^{---} \rightarrow [\mathrm{Co(CN)_6}]^{--}$ is irreversible at the dropping electrode, the process $[\mathrm{Pd(CN)_4}]^{--} \rightarrow \mathrm{Pd} + 4\mathrm{CN^-}$ is reversible, although it involves the total disruption of a stable complex.

No indication was found of the formation of monovalent platinum and palladium cyanide complexes, which were prepared by Manchot and Schmid[11] by reduction of the bivalent complexes with sodium amalgam. These compounds, like the analogous $\mathrm{Ni^I}$ and $\mathrm{Co^I}$ complexes, do not seem to be stable under polarographic conditions.

The fact that the complex cyanides of $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ are not reducible at the dropping electrode is in agreement with their known similarity in structure and properties to the ferrocyanides, which also are not reducible polarographically.

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(9) Private communication from F. P. Dwyer.

(10) Sidgwick, *J. Chem. Soc.*, 433 (1941).

(11) Manchot and Schmid, *Ber.*, **63**, 2775, 2782 (1930).

Summary

1. Of the five metals studied in the present work, *viz.*, ruthenium, osmium, iridium, palladium and platinum, only palladium gave satisfactory polarographic steps.

2. Palladium complexes in general are reducible at the dropping electrode giving one step which corresponds to direct reduction of Pd^{II} to Pd. Various supporting electrolytes which form complexes with the metal are suitable for its analytical determination.

3. In complexes of palladium with amines, the half-wave potential becomes more negative with increasing basic strength of the amine, *i. e.*, the complexes become more resistant to reduction. At the same time the reduction becomes less reversible.

4. The relative stabilities of the complex cyanides of Group VIII are discussed in the light of their polarographic behavior.

SYDNEY, AUSTRALIA RECEIVED DECEMBER 27, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Effect of Nitric Oxide upon the Biacetyl Promoted Thermal Decompositions of Acetone and Acetaldehyde

BY CHARLES H. KLUTE[1] AND W. D. WALTERS

Earlier studies[2,3] have shown that nitric oxide often has a considerable effect upon the thermal decompositions of organic compounds. Verhoek[2] observed that nitric oxide catalyzed the thermal decompositions of acetaldehyde, trichloroacetaldehyde, and chloroform. Later Staveley and Hinshelwood[3a] and also other investigators[3b,c] demonstrated that nitric oxide exerts an inhibiting influence on the decompositions of ethers, hydrocarbons, and certain aldehydes.

Subsequent investigations have indicated that nitric oxide may not always be a satisfactory inhibitor. Although it was observed that nitric oxide did not inhibit the thermal decompositions of acetone and acetaldehyde,[3a] Rice and Polly[4a] found that the rates of pressure increase in these decompositions can be considerably reduced by the addition of propylene. Rice and Polly observed also that ethyl nitrite, which produces nitric oxide upon decomposition, has only a relatively small effect upon the oxygen promoted decomposition of acetaldehyde occurring during the first few seconds at 500°. Moreover, nitric oxide does not inhibit the hydrogen sulfide catalyzed acetaldehyde decomposition.[4b] In the decomposition of *n*-butane induced by ethylene oxide, Steacie and Folkins[5] showed that not all of the chains are stopped by nitric oxide.

Recently Smith and Hinshelwood[6] by analyzing chemically for undecomposed aldehyde have confirmed the fact that the acetaldehyde decomposition is much slower in the presence of propylene than in the presence of nitric oxide. Concerning this inhibition by propylene Morris[7] has concluded that the inhibition involves only an induced decomposition which is superimposed upon the true unimolecular process. However, irrespective of differences in interpretation of the propylene inhibition it is significant that in the presence of certain carbonyl compounds nitric oxide may not be an efficient inhibitor. Therefore, in order to investigate further the effectiveness of nitric oxide as a chain inhibitor, a study of the influence of nitric oxide upon the biacetyl promoted decompositions of acetone and acetaldehyde was undertaken.

Experimental

Apparatus and Method.—The reaction vessel, a cylindrical Pyrex bulb, 61 × 135 mm., was contained in a steel cylinder, and the furnace was heated electrically by the use of Nichrome resistance wire wound around the asbestos-covered steel cylinder. The temperature of the furnace was automatically controlled as in an earlier study,[8] and a chromel–alumel thermocouple connected to a potentiometer was used to measure the temperature. During a run the temperature was maintained constant to within ±0.3°, and the accuracy of the temperature measurements should be at least ±1 since the chromel–alumel thermocouples, standardized at the sulfur boiling point,[9] were replaced frequently.

In the case of the acetaldehyde decomposition it has been observed that traces of oxygen accelerate the decomposition and that the rate of the decomposition is faster in a reaction vessel freshly cleaned with nitric acid or in a vessel evacuated exhaustively.[10] However, Leifer and Urey[11] found that only by oxygen treatment followed by diffusion pumping could the walls of the reaction vessel be freed completely of the nitric oxide used in a previous experiment. Therefore, in the present investigation the following procedure was adopted. Runs were made in the following order: (a) acetaldehyde, (b) acetaldehyde and biacetyl, (c) acetaldehyde, biacetyl, and nitric oxide. Before the rate of decomposition of pure acetaldehyde was

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(1) Fellow of the Sherman Clarke Fund for Chemical Research, University of Rochester.

(2) Verhoek, *Trans. Faraday Soc.*, **31**, 1521, 1533 (1935).

(3) (a) Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **154A**, 335 (1936); **159A**, 192 (1937); *J. Chem. Soc.*, 1568 (1937); (b) Hobbs and Hinshelwood, *Proc. Roy. Soc.* (London), **167A**, 439, 447 (1938); (c) Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

(4) (a) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938); (b) Roth and Rollefson, THIS JOURNAL, **64**, 1707 (1942).

(5) Steacie and Folkins, *Can. J. Research*, **17B**, 105 (1939).

(6) Smith and Hinshelwood, *Proc. Roy. Soc.* (London), **180A**, 237 (1942); similar work with acetone, *ibid.*, **183A**, 33 (1944).

(7) Morris, THIS JOURNAL, **66**, 584 (1944).

(8) Gantz and Walters, *ibid.*, **63**, 3412 (1941).

(9) Mueller and Burgess, *Bur. Standards Sci. Pap.*, **15**, 163 (1919), S 339.

(10) Letort, *J. chim. phys.*, **34**, 265, 355, 423 (1937).

(11) Leifer and Urey, THIS JOURNAL, **64**, 995 (1942).