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

The Interaction of Platinum(II) and Tin(II) Chlorides[1]

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An extensive study has been made of the reaction between platinum(II) and tin(II) chlorides, in hydrochloric acid solution, in which a soluble product of intense red color is formed. The colored reaction product was very soluble in the higher alcohols; the distribution ratio between methyl-*n*-hexylcarbinol (capryl alcohol) and aqueous hydrochloric acid was about 20,000. Distribution equilibrium studies, followed by chemical analysis of the two phases for tin and platinum, showed that the extracted product corresponded to a tin to platinum reaction ratio of 3:1. Application of the spectrophotometric method of continuous variations indicated the existence of several reaction products. The method of mole ratios established the existence of complexes the formation of which involved tin to platinum ratios of 1:4, 1:2, 1:1, 3:2, 2:1, 3:1 and 5:1. Some of the reactions were very slow, others rapid. In aqueous medium, the principal product corresponded to a tin to platinum ratio of 5:1. In this reaction, one mole of tin(II) was oxidized to tin(IV) simultaneously with reduction of platinum(II) to platinum(0). Precipitation tests showed a product containing four moles of tin(II) and four moles of chloride ion associated with one platinum, in the form of a tetrapositive ion, $[PtSn_4Cl_4]^{++++}$, in which the platinum exists in zero oxidation state.

Early reports[2–4] of the reaction of compounds of platinum with tin(II) in solution have varied widely in regard to color and solubility of product, and reaction stoichiometry. Wöhler and Spengel[5] reported continuous increase of brown color on addition of tin(II) to platinum chloride, and no definite stoichiometry; the product was soluble in certain organic solvents, and was reported not to pass through semi-permeable membranes. They concluded that the product was colloidal platinum, and that the reaction was not suitable for colorimetric determination of platinum. Other authors[6–10] have found the reaction to give rapid formation of stable yellow to red solutions suitable for colorimetric estimation. The color has been attributed to platinum(II)[10] and to chloroplatinous acid.[11,12] In a spectrophotometric study of the platinum(IV)-tin(II) chloride system, Ayres and Meyer[13] obtained red solutions the absorption spectra of which in no way resembled those cited by Wöhler and Spengel[5]; the properties of the solutions were not compatible with the presence of colloidal platinum nor of chloroplatinous acid, and it was shown that chloride ion was necessary for the color formation.

In the experimental work reported below, extraction equilibria studies indicated the existence of a product of 3:1 tin to platinum mole ratio, and spectrophotometric methods and precipitation tests indicated the presence of a cationic complex containing platinum(0), tin(II) and chloride, to which the formula $[PtSn_4Cl_4]^{++++}$ has been tentatively assigned.

Experimental

Reagents.—Standard platinum(IV) solution was prepared by dissolution of grade No. 1 platinum thermocouple wire (99.99% pure) in aqua regia, followed by repeated evaporation with hydrochloric acid, then dilution to known volume.

Platinum(II) chloride was prepared from chloroplatinic acid as described by Kharasch and Ashford.[14]

Potassium tetrachloroplatinate(II), K_2PtCl_4, was purchased (Fisher Scientific Co.) and some was also prepared from platinum(II) chloride and potassium chloride.

Tin(II) chloride stock solution was approximately 2 *M* in this compound and 3.6 *M* in hydrochloric acid; metallic tin was added and the solution was stored under carbon dioxide. Solutions of lower concentration were prepared as needed by dilution with deaerated 3.6 *M* hydrochloric acid, and were standardized titrimetrically with iodide-iodate solution.

Phenylarsonic acid was prepared as has been described by Welcher.[15]

Methyl-*n*-hexylcarbinol (capryl alcohol), Eastman Kodak Co. No. 66, was used for the extractions; the practical grade was satisfactory.

Standard solutions of the various titrants were prepared from reagent grade chemicals and were standardized by conventional methods.

Apparatus.—Absorbance measurements were made with a Beckman model DU spectrophotometer, with tungsten source for the visible region and hydrogen discharge lamp for the ultraviolet region. A positive pressure of carbon dioxide was maintained in the cell compartment to prevent oxidation of the tin(II) during measurements, which were made at 30 ± 0.5° in 1.000-cm. silica cells; for measuring solutions of very high absorbance, silica inserts were used to give optical paths of 0.105 cm. or 0.0056 cm.

Mixing of reagents and transfer of the solution to the spectrophotometer cell was accomplished by apparatus described by Roberts and Field[16] except that the absorption cell was attached by a ground glass joint.

Extractions were made at 30 ± 0.5° in a specially constructed cylindrical separatory funnel which provided for stirring, removal of samples of either layer, and maintenance of carbon dioxide atmosphere.

Absorbance Ratio.—When applied to the platinum(II)-tin(II) chloride system, the absorbance ratio method[17–19] gave ratios varying widely with the wave length at which measurements were made, indicating that at least two

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[1] This work was supported jointly by The United States Atomic Energy Commission and The University of Texas, under Contract No. AT-(40-1-)-1037.

[2] R. J. Kane, *Phil. Mag.*, [3] **7**, 399 (1835).

[3] R. Schneider, *Poggendorff's Ann.*, **136**, 105 (1869).

[4] M. A. Ditte, *Ann. chim. phys.*, **27**, 145 (1882).

[5] L. Wöhler and A. L. Spengel, *Z. Chem. Ind. Kolloide*, **7**, 249 (1909).

[6] N. A. Figurovskii, *Ann. secteur platine, Inst. Chim. gen.* (U.S.S.R.), No. 15, 129 (1938); *C. A.*, **33**, 2065 (1939).

[7] N. S. Poluektov and F. G. Spivak, *Zavodskaya Lab.*, **11**, 398 (1945).

[8] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1944, pp. 358–360.

[9] S. O. Thompson, F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 420 (1937).

[10] D. Hunter, R. Milton and K. M. A. Perry, *Brit. J. Ind. Med.*, **2**, 92 (1945).

[11] N. H. Furman, ed., "Scott's Standard Methods of Chemical Analysis," Vol. I, D. Van Nostrand Co., New York, N. Y., 5th ed., 1939, p. 713.

[12] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 9th ed., 1937, p. 523.

[13] G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, **23**, 299 (1951).

[14] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1736 (1936).

[15] F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., New York, N. Y., 1948, pp. 53–54.

[16] G. L. Roberts and F. H. Field, THIS JOURNAL, **72**, 4232 (1950).

[17] J. Molland, *ibid.*, **62**, 541 (1940).

[18] H. E. Bent and C. L. French, *ibid.*, **63**, 568 (1941).

[19] A. E. Harvey and C. L. Manning, *ibid.*, **72**, 4488 (1950).

colored products of different spectral characteristics were formed.

Method of Continuous Variations.—The method[20,21] was applied first using hexachloroplatinate(IV) and tin(II) chloride in 1.2 *M* hydrochloric acid. Spectral curves over the range 320 to 450 mμ, for solutions in which the tin to platinum mole ratio varied from 0:1 to 8:1, showed no ideal wave lengths for making the measurements for the method of continuous variations. Solutions were prepared in which the total molar concentration of reactants was 0.0010; all solutions were 1.2 *M* in hydrochloric acid. Absorbances were measured at nine different wave lengths from 320 to 450 mμ; six representative curves are shown in Fig. 1. The curves minimizing at 0.5 mole fraction of tin correspond to a 1:1 mole ratio in the reaction, and represent the reduction of platinum(IV) to platinum(II), as was shown by the similarity of the spectral curves of the reaction mixture and a solution containing only tetrachloroplatinate(II).

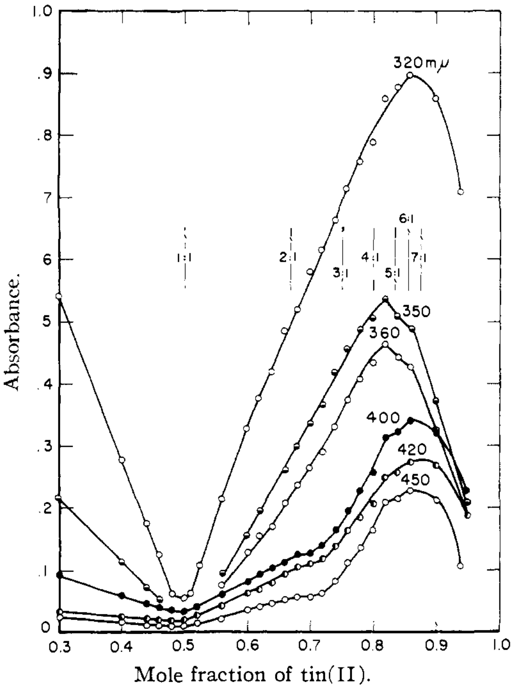

Fig. 1. Continuous variations method, platinum(IV)–tin(II) system; platinum(II) gave curves similar to the above to the right of the minima, except for displacement corresponding to one less mole of tin(II) per mole of platinum.

The experiments were repeated, using tetrachloroplatinate(II) as the source of platinum. The curves of absorbance plotted against mole fraction of tin(II) were similar to those of Fig. 1 to the right of the minima, except that the maxima occurred at mole fractions corresponding to one mole less of tin per mole of platinum. Although the curve maxima and the change of slope gave some indication of the reaction ratio of tin to platinum(II) (*e.g.*, 2:1, 3:1, 5:1), the continuous variations method does not give unambiguously the stoichiometry of the higher ratio, more highly colored complexes. It seems clear, however, that platinum(IV) is first reduced to platinum(II), which then reacts with two or three moles of tin(II) to form a colored product; on further addition of tin(II), additional species of greater color intensity and higher tin to platinum stoichiometry are indicated.

Mole Ratio Method.—Determination of the composition of complexes in solution by the mole ratio method[19,22] has been extended in the present study to cases in which more than one product is formed under given conditions.

Addition of a small amount of tin(II) chloride solution to the platinum(II) solution produced first a pink-yellow color; at a tin to platinum ratio of 0.5:1, an intense yellow color developed rapidly. At a 1:1 ratio the solution was yellow-orange, and showed gradations from orange to deep red as the ratio was increased to 5:1 or higher. All solutions of ratio less than 5:1 showed further color development on standing; changes were most noticeable when the ratio was about 1.5:1, in which case a brown color developed in 20 to 30 minutes, and after one or two days the solutions were so opaque that the absorbance for 1 cm. thickness could not be measured at wave lengths below 700 mμ. Addition of excess tin(II) slowly converted the brown solutions to clear deep red solutions. The brown product did not pass through semi-permeable membranes, whereas the red solutions did pass through. The increase in absorbance of the solutions continued for several weeks; slight precipitates developed after about three weeks in solutions of mole ratios between 0.5:1 and 2:1. On heating, the absorbance of all solutions increased rapidly; by heating for several hours, most of the colored material in solutions of mole ratio less than 1:1 was precipitated; solutions of mole ratio greater than 2:1 gave no precipitate when heated.

Upon exposure to air, all of the deeply colored solutions faded to the color characteristic of platinum(II), as the tin (II) became air-oxidized. The brown solutions changed more slowly than the others, but were oxidized rapidly by hydrogen peroxide, with no gas evolution. Precipitates were not dissolved, either by excess tin(II) or by hydrogen peroxide; the latter was decomposed catalytically.

Solutions in which the tin(II) to platinum(II) ratio was varied from 1:10 to 6:1 were prepared and their absorbances measured over the wave length region 250 to 600 mμ; solutions of very high absorbance were measured in cells of 0.105 or 0.0056 cm. optical path. Measurements on each solution were made as rapidly as possible for about two hours, and were continued at intervals for several weeks. These measurements indicated the existence of both rapid and slow reactions in the system. Interest was centered on the initial rapid reaction, hence, for application of the mole ratio method it was necessary to eliminate, as far as possible, any contribution of the slower reactions to the measured absorbance. In the region 250 to 325 mμ, absorbance of the fast-reaction products was large, whereas above about 600 mμ the slow-reaction products made the principal contribution to the absorbance after several minutes. By constructing absorbance *versus* time curves for the various reaction mixtures measured at several wave lengths, it was possible to extrapolate the measured absorbances back to values which represented virtual completion of the fast reactions and little or no contribution of the slower reactions. From the corrected absorbance, results were calculated to molar absorptivity. Figure 2 shows a plot of molar absorptivity against wave length for solutions of several mole ratios of tin to platinum. The spectral curves for solutions of the composition of suspected complexes are shown as solid lines; intermediate ratios are shown as broken lines.

Molar absorptivity at a given wave length was plotted against mole ratio of tin to platinum; experimental points were joined by straight lines in best agreement. Representative curves are shown in Figs. 3 to 6; breaks in the curves correspond to reactions between one mole of platinum(II) and 0.25, 0.5, 1, 1.5, 2, 3 and 5 moles of tin(II). The probable error of a single measurement was estimated to be about 2%. The maximum effects of deviations from Beer's law, when measurements are made in spectral regions of rapidly changing absorbance, or when wide slit settings are required[23] were not sufficient to account for the breaks in the mole ratio curves; real reactions were indicated.

Increases in absorbance were observed when more tin(II) was added to solutions of mole ratio 5:1; it was not possible to determine whether the increased absorbance, at the shorter wave lengths, was caused by a suppressed dissociation of the product of 5:1 ratio, or was due to the formation of a product involving a 6:1 ratio.

Extraction Studies.—Qualitative tests with many organic liquids showed that little or no extraction resulted from the use of ethers, esters, acids, aldehydes, hydrocarbons and halogenated hydrocarbons; ketones and alcohols gave virtually complete extraction. The partition coefficient, un-

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[20] P. Job, *Ann. chim.* (*Paris*), [10] **9**, 113 (1928).

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

[22] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 111 (1944).

[23] C. F. Hiskey and I. G. Young, *Anal. Chem.*, **23**, 1196 (1951).

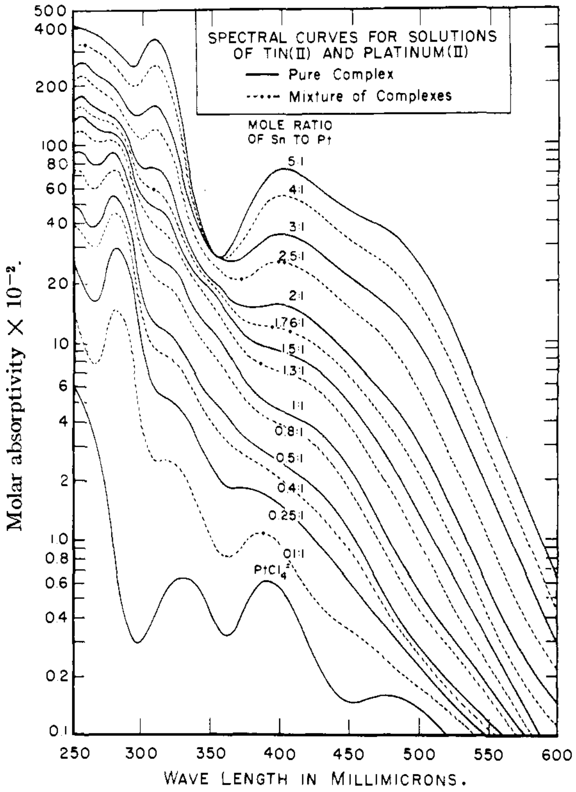

Fig. 2.

der optimum conditions, was about 20,000:1 between methyl-*n*-hexylcarbinol (capryl alcohol) and the aqueous solution. Spectral curves of the product in the two solvents were practically identical.

Measurements of extraction equilibria offered two possibilities for the study of the reactions. First, by determining the distribution coefficient of tin(II) chloride in the absence and then in the presence of platinum(II), the stoichiometry of the complex in the organic layer might be determined. Second, the concentration of the complex in the aqueous layer would be constant and determinable, *i.e.*, equal to the equilibrium concentration of the platinum in the aqueous layer at high tin concentrations; hence, by varying the concentration of tin(II) in the aqueous layer and measuring the resulting changes in the tin and the platinum concentrations, the stoichiometry of the reaction in aqueous medium might be deduced. Application of the second method involves the assumptions that the activity coefficients of reactants are constant at the high constant concentration of indifferent electrolyte and relatively small changes in tin concentration, and that unreacted platinum(II) and any other complexes formed are not appreciably extracted; the latter was checked by separate measurement of the extractability of platinum(II) and by material balances for the platinum and tin after each addition of reagents.

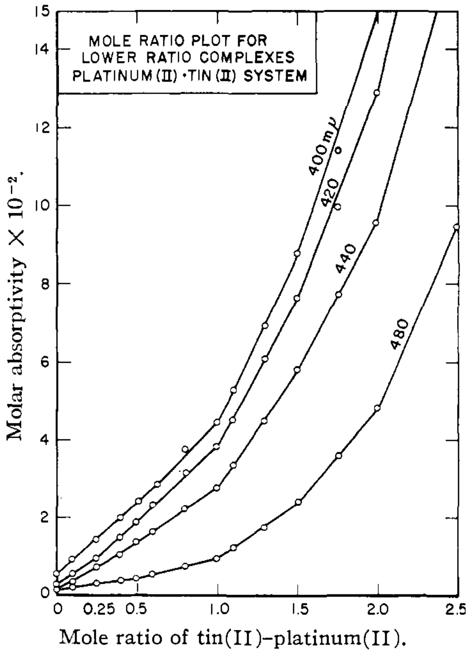

Fig. 3.

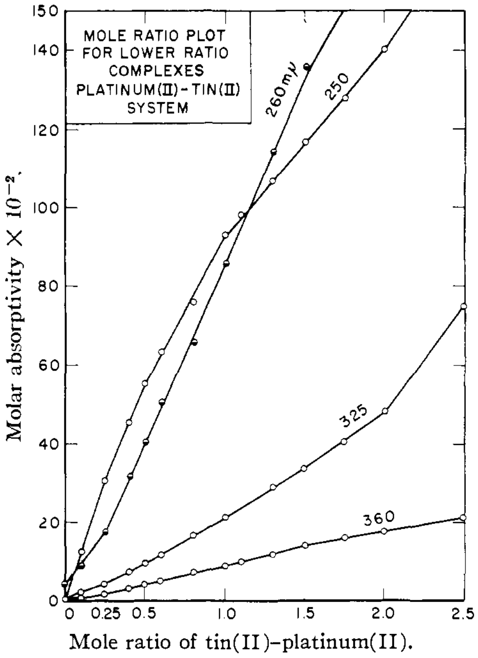

Fig. 4.

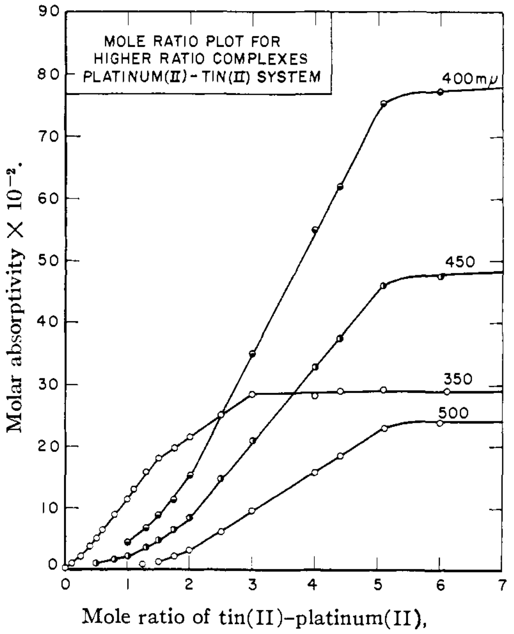

Fig. 5.

A solution 2.5 M in tin(II) and 3.6 M in hydrochloric acid was shaken with capryl alcohol presaturated with 3.6 M hydrochloric acid. Aliquot samples from each layer

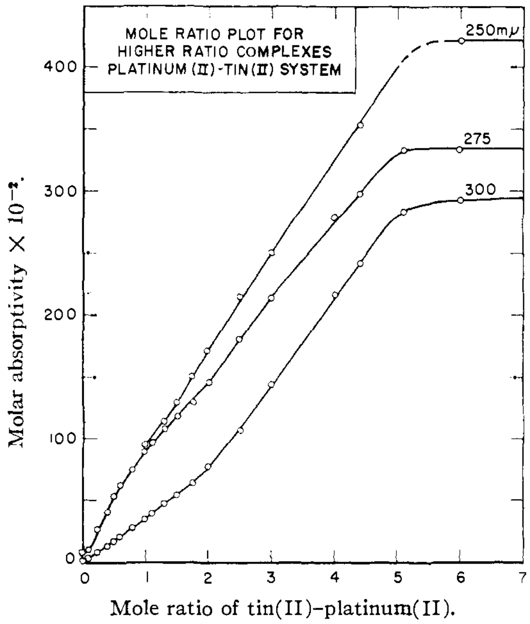

Fig. 6.

were analyzed for tin(II) by titration with standard iodide-iodate solution; shaking of the mixture and analysis of aliquots was repeated until successive determinations agreed to 0.5%; extraction equilibrium was attained rapidly. The concentration of tin(II) was then decreased by adding either fresh organic solvent or 3.6 *M* hydrochloric acid, and the equilibrations and analyses were repeated; the process was continued for thirty dilutions. A plot of tin(II) concentration in the organic layer against tin(II) concentration in the aqueous layer, on log-log coördinates to cover the wide ranges, was nearly linear.

A solution of tin(II) chloride, 3.6 *M* in hydrochloric acid, was equilibrated with capryl alcohol; solid platinum(II) chloride was added in an amount to give a known concentration in the organic layer. The aqueous layer was sampled and analyzed for tin(II), and the corresponding equilibrium concentration of tin(II) in the organic layer was determined from the distribution plot. From the decrease in total tin(II) concentration, the number of moles of tin associated with one mole of platinum was found to be 2.92. After the tin(II) concentration had been decreased by successive equilibrations with diluting solution, the organic layer was sampled and analyzed for total reducing capacity at two lower tin concentrations. The analyses, calculated to moles of tin per mole of platinum, were 3.08 and 3.16. It was concluded that a reaction product of 3:1 stoichiometry was the predominant species which extracted into the organic solvent.

Hydrolytic Precipitation.—A known weight of potassium tetrachloroplatinate(II) was dissolved in a measured amount of tin(II) chloride solution, in excess of a 6:1 ratio to the platinum. The mixture was treated with excess carbonate-free 50% sodium hydroxide solution, which held the tin in solution. The dark brown precipitate was removed by centrifugation, and aliquots of the supernatant solution were acidified and analyzed for tin(II). An identical amount of tin(II) chloride solution was carried through the same steps as a control; the difference in the two titrations represented tin which had been precipitated with the platinum. Duplicate runs, calculated to the basis of moles of tin per mole of platinum, gave ratios of 4.93:1 and 4.92:1, in good agreement with the 5:1 reaction stoichiometry previously indicated in aqueous solution by the spectrophotometric mole ratio method. The brown precipitates, if treated promptly with hydrochloric acid, dissolved readily to give red solutions identical with the original solutions.

Precipitation by Phenylarsonic Acid.—Phenylarsonic acid, in solutions of proper acidity, selectively precipitates tetrapositive ions. A solution 0.6 to 0.7 *M* in hydrochloric acid was used in the following tests.

Addition of platinum(II) solution to the acidic solution containing excess tin(II) and phenylarsonic acid, or addition of phenylarsonic acid to the mixture of platinum(II) and tin(II), gave a voluminous yellow precipitate containing all of the platinum. The precipitate dissolved in 2 *M* hydrochloric acid to give a dark brown solution; when the acidity was increased to 4 *M*, the solution returned to the dark red color characteristic of the platinum-tin reaction. From the decrease in tin(II) concentration of the solution as a result of the precipitation, calculation to the basis of moles of tin(II) per mole of platinum gave a ratio of 5.1:1.

Precipitations with phenylarsonic acid indicated the presence of a tetrapositive ion containing the platinum. Furthermore, if the reaction between platinum(II) and tin(II) involved oxidation-reduction, the tin(IV) produced should be precipitable with phenylarsonic acid. Solutions in which the tin(II) to platinum(II) ratio was varied from an excess to a deficiency of tin(II) for a 5:1 ratio, were fractionally precipitated with definite increments of phenylarsonic acid. The amount of platinum remaining unprecipitated after each increment of phenylarsonic acid was determined, and compared with the calculated amount on the assumption of the 5:1 ratio in the reaction. After complete precipitation of the platinum compound with phenylarsonic acid, additional increments of phenylarsonic acid precipitated white tin(IV) phenylarsonate. The experimental results were in good agreement with the 5:1 mole ratio in the tin-platinum reaction, and the formation of one mole of tin(IV) by oxidation.

Determination of Chloride in the Complex.—A control sample containing tin(II) chloride, phenylarsonic acid and hydrochloric acid was analyzed in parallel with an identical solution to which a known amount of platinum(II) was added; the phenylarsonate precipitate was removed by centrifugation, and the solution was analyzed for chloride; the chloride content of the phenylarsonate precipitate was obtained by difference. The mole ratio of chloride to platinum in the precipitate was 4:1.

Two samples, each containing 0.100 mmole of platinum, were treated with 0.500 mmole of tin(II) and 0.500 mmole (an excess) of phenylarsonic acid, in sufficient hydrochloric acid to prevent precipitation. The acidity was then decreased by dilution to about 0.5 *M* in acid, to allow precipitation to occur. The precipitates were washed, and dried to constant weight, 173.5 and 171.9 mg.; the average corresponds to a "molecular weight," based upon the platinum taken, of 1727. In the 5:1 mole ratio reaction, previous tests showed that one mole of tin(IV) was formed, and the complex containing the platinum and the remaining tin(II) as well as 4 chlorides, was precipitated by phenylarsonic acid, as was also the tin(IV). The precipitate obtained with excess phenylarsonic acid would therefore have the composition $[\mathrm{PtSn_4Cl_4}](\mathrm{C_6H_5AsO_3})_2 + \mathrm{Sn}(\mathrm{C_6H_5AsO_3})_2$, for which the combined molecular weights is 1730.

Discussion

In the interaction of one mole of platinum(II) with 5 moles of tin(II), one tin(II) was oxidized to tin(IV); since platinum(II) was the only reducible substance present, it is assumed to have been reduced to platinum(0); the remaining four atoms of tin(II) were present in the colored product. The oxidation states of the metals in the product correspond to a deficiency of eight electrons. Two moles of phenylarsonic acid, which precipitated the product, would form four salt-type bonds. Electrical neutrality of the phenylarsonate precipitate would require the presence of four equivalents of anion in the cationic aggregate; analysis for chloride in the precipitate showed these anions to be four chlorides. It is deduced, therefore, that the colored product in the aqueous solution contains a tetrapositive ion, $[\mathrm{PtSn_4Cl_4}]^{++++}$, or perhaps its chloride compound, in which the platinum exists in zero oxidation state.

Two classes of compounds are known which represent similar unusual oxidation states: tetracyanonickelate(0)[24] and tetracyanopalladate(0)[25] in which the metals are combined in zero oxidation state; and the lower halide complexes of tantalum and niobium, which contain metallic bonds.[26] From the position of platinum in the periodic system, it would appear more reasonable to place the compound in the first class, but some of its properties are more like those of the second class, which are colored, stable in aqueous solution, and highly soluble in ethanol. Chemical evidence at hand is insufficient to warrant an attempt to explain the manner in which the platinum, tin and chlorine are bound in the complex.

Very little evidence was obtained about the lower ratio reaction products and the products of the slow reactions; it is possible that these species may exist as polymers. As yet, it has not been possible to isolate any of the products in crystalline form for making X-ray examination. At least two of the other platinum metals, palladium and rhodium, react in solution with tin(II) chloride to form colored products the properties of which are not compatible with the formation of colloidal metals; a thorough study of these reactions might serve to clarify the observations made on the platinum system.

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[24] J. W. Estes and W. M. Burgess, THIS JOURNAL, **64**, 2715 (1942).

[25] J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

[26] P. A. Vaught, J. H. Sturdivant and L. Pauling, *ibid.*, **72**, 5477 (1950).

[CONTRIBUTION OF BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES]

The Dissociation of Iron Pentacarbonyl in Certain Amines

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Evidence for the dissociation of iron pentacarbonyl in certain amines according to $2Fe(CO)_5 \rightleftarrows [Fe(CO)_6]^{++} + [Fe(CO)_4]^-$ is presented and the effect of amine structure on this reaction discussed.

In connection with studies on the mechanism of catalysis by metal carbonyls and hydrocarbonyls, the reaction of iron pentacarbonyl with certain amines was investigated.

It was found that when iron pentacarbonyl is dissolved in piperidine, the solution becomes warm; at the same time it becomes conducting, indicating that ions have been formed. As no carbon monoxide is evolved on mixing of the two compounds and as the solution is diamagnetic, ionization does not involve the formation of ferrous or ferric ions. A postulate consistent with these facts and with the tendency of the metal carbonyls to form structures having the rare gas configuration is that iron pentacarbonyl dissociates in piperidine according to equation 1

$$2Fe(CO)_5 \rightleftarrows \underset{\text{I}}{Fe(CO)_6^{++}} + \underset{\text{II}}{[Fe(CO)_4]^-} \quad (1)$$

The effective atomic number of iron in iron pentacarbonyl and in both of the ions I and II is 36, which corresponds to the electronic configuration of krypton. Whereas the existence of anion II in its salts[1] has been described, no prior evidence has been shown for the existence of the positively charged iron carbonyl complex I.

The infrared spectrum of iron pentacarbonyl in piperidine corroborates the presence of these ions. The spectrum of $Fe(CO)_5$ in cyclohexane solution contains two bands[2] in the $C\equiv O$ triple bond region at 2022 and 2000 cm.$^{-1}$. Both bands disappear when $Fe(CO)_5$ is dissolved in piperidine; in their place appear two new bands at 1898 and 2016 cm.$^{-1}$. The band at 1898 cm.$^{-1}$ may be attributed to II in view of the fact that cobalt carbonyl anion, $[Co(CO)_4]^-$, which is isoelectronic with II, gives rise to a single band located at the same position.[2] By elimination, the band at 2016 cm.$^{-1}$ must be due to I.

The fact that I and II each give rise to a single band is in agreement with group theory[3] which predicts a single infrared active $C\equiv O$ stretching frequency for an octahedral[4] as well as a tetrahedral[5] metal carbonyl. These predictions were verified in the case of chromium carbonyl,[4] $Cr(CO)_6$, which has an octahedral configuration,[6] and in the case of nickel carbonyl,[5] $Ni(CO)_4$, which possesses a tetrahedral configuration.[7] That I possesses an octahedral and II a tetrahedral configuration is likely as I is isoelectronic with $Cr(CO)_6$ and II is isoelectronic with $Ni(CO)_4$.

The Effect of Amine Structure on the Dissociation of $Fe(CO)_5$.—An insight into the mechanism of the dissociation of iron pentacarbonyl in piperidine may be secured from the conductivity of iron pentacarbonyl in various amines. The data in Table I show that the ability of an amine to cause ionization of iron pentacarbonyl is dependent on two main factors: (a) The availability of the lone pair of electrons on nitrogen for bonding or charge neutralization, a polar effect; and (b) the presence of many or bulky substituents on nitrogen which pre-

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[1] H. Hock and H. Stulmann, *Ber.*, **61**, 2097 (1928); F. Feigl and P. Krumholz, *Z. anorg. allgem. Chem.*, **215**, 242 (1933); P. Krumholz and H. M. A. Stettiner, THIS JOURNAL, **71**, 3035 (1949).

[2] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, unpublished work.

[3] The applications of group theory to the determination of molecular structure are described by Gerhard Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[4] R. A. Friedel, S. L. Shufler and H. W. Sternberg, unpublished work.

[5] B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938).

[6] L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

[7] J. Ladell, B. Post and I. Fankuchen, *Acta Cryst.*, **5**, 795 (1952).