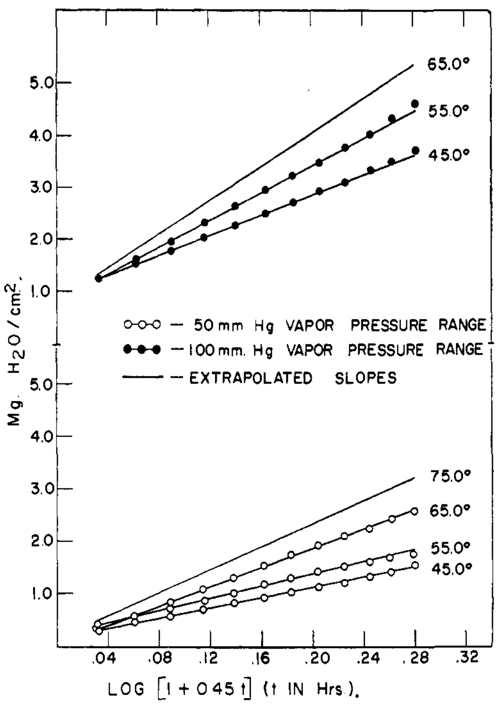

Fig. 2.—Logarithmic plot of water vapor data in two pressure ranges.

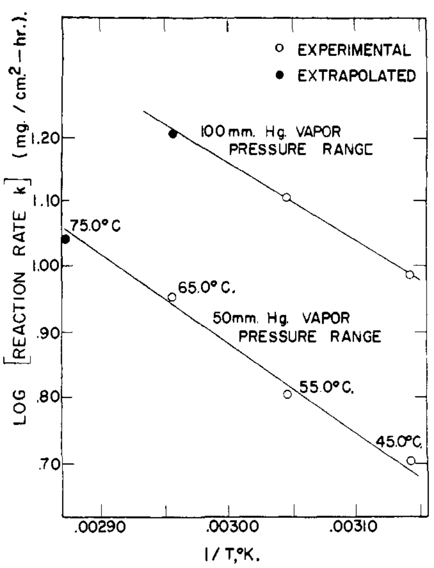

Fig. 3.—Log *k* *vs.* 1/*T* from water vapor–lithium data; each point represents the mean of several determinations.

and Cubicciotti.[7] These workers derived the equation from Fick's law following the method of Tammann and Koster,[9] assuming that the logarithmic oxidation was related to a vitreous oxide product. Therefore, it was interesting to note that in the reaction of lithium with water vapor, a glassy black coat always appeared on the metal surface at the beginning of the reactions. This black coat remained for a period of time depending on the temperature and water vapor pressure, and then slowly changed to a white material. Analysis of both the white and black material by means of an X-ray diffractometer indicated that the only compound present was LiOH. However, the glassy black coat was characterized in the X-ray patterns by broad peaks and absences of some reflections, indicating that a completely crystalline hydroxide was not formed during this stage of the reaction. Following the suggestion of Cubicciotti and Brodsky[7] this lack of crystallinity of the LiOH coat could be responsible for the logarithmic rate law observed for these data.

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[9] G. Tammann and W. Koster, *Z. anorg. allgem. Chem.*, **123**, 196 (1922).

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

Evidence for the Existence of an Ammine of Platinum(0)[1]

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The reduction of tetrammineplatinum(II) bromide with potassium in liquid ammonia at its boiling point is best interpreted as involving the addition of two electrons to the 4-coplanar tetrammineplatinum(II) ion to form a neutral tetrammine of platinum(0). Decomposition of this product yields only ammonia and platinum; the latter is an effective catalyst for the hydrogenation of olefins. The interaction of tetrammineplatinum(II) bromide and potassium amide in liquid ammonia yields platinum(II) amide 2-ammonate.

The reduction of salts of transitional metals by means of solutions of alkali metals in liquid ammonia typically results in *rapid* reduction to the elemental metals, in some cases accompanied by products of competing reactions, *e.g.*, amides, imides and/or nitrides.[2–5] The principal ammonia-insoluble product is usually a black finely divided solid that is pyrophoric and an excellent catalyst for the conversion of alkali metals to the corresponding amides and for the hydrogenation of olefins.[5]

The reduction of tetrammineplatinum(II) bromide, however, with potassium in liquid ammonia at −33.5° proceeds relatively slowly without evolution of water-insoluble gases and results in the precipitation of a yellowish-white voluminous solid that does not catalyze appreciably the formation of potassium amide. Although this primary reduction product ultimately decomposes to yield finely divided elemental platinum which is an excellent catalyst for alkali amide formation and for

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] G. W. Watt, *Chem. Revs.*, **46**, 289 (1950).

[3] G. W. Watt and W. A. Jenkins, Jr., THIS JOURNAL, **73**, 3275 (1951).

[4] G. W. Watt and C. W. Keenan, *ibid.*, **74**, 2048 (1952).

[5] G. W. Watt, W. F. Roper and S. G. Parker, *ibid.*, **73**, 5791 (1951).

olefin hydrogenation, it appears that the initial reduction reaction is best interpreted as involving the formation of tetrammineplatinum(0) even though it has not been possible to demonstrate that the ammonia-to-platinum ratio is as great as 4/1.

Both potentiometric[6] and conductimetric titrations of liquid ammonia solutions of tetrammineplatinum(II) bromide with standard solutions of potassium in liquid ammonia clearly demonstrate that the formation of this product requires the addition of exactly two gram-atoms of potassium per mole of the bromide and that subsequent reactions involving excess potassium occur only extremely slowly. Analysis of the combined supernatant solution and washings accounts for substantially all of the potassium and bromide ions.

Thermal decomposition of the initial reduction product, which occurs at or below 25°, produces *only* gaseous ammonia and elemental platinum.[7] All efforts to establish the exact decomposition temperature were unsuccessful. Owing to the inherent instability of this product and to the difficulty of distinguishing between bound ammonia and that comprising the medium in which the solid is formed, the measured ratios of ammonia to platinum are always less than that corresponding to $Pt(NH_3)_4$.

That the primary ammonia-insoluble reduction product must consist of tetrammineplatinum(0) is nevertheless supported by the data given below and is also reasonable in terms of Pauling's generalizations relative to the stability of coördination compounds of the transitional elements,[8] *i.e.*

$$[Pt(NH_3)_4]^{2+} + 2Br^- + 2K^+ + 2e^- \longrightarrow 2KBr + [Pt(NH_3)_4]^0$$

The coördination of the four ammonia molecules in the tetrammineplatinum(II) ion is known to involve a 4-coplanar configuration of the dsp^2 type.[9] The addition of two electrons to the vacant 6p orbital leads to a neutral species in which platinum has an effective atomic number (86) equal to that of the next inert gas, radon. Tetrammineplatinum(0) therefore should be expected to exhibit an appreciable stability,[8] whereas there is no apparent reason why a diammine (most clearly indicated by the analytical data) should be stable. The tetrammine would be analogous to other well-established cases of compounds of elements in zero oxidation states, *e.g.*, potassium cyanonickelate(0),[10] potassium cyanopalladate(0),[11] potassium tetracyanocobaltate(0)[12] and indeed to the familiar nickel tetracarbonyl.

Similar reduction reactions have been carried out using *trans*-dibromodiammineplatinum(II) as the starting material. In liquid ammonia at −33.5°, or by reaction between ammonia gas and the solid at 25°, this compound is slowly converted to tetrammineplatinum(II) bromide[13] and if sufficient time is allowed for completion of this conversion the results of the reduction reaction are of course the same as indicated above.

In order to establish that the ammonia-insoluble reduction product does not arise from reactions involving potassium amide, the action of this base upon tetrammineplatinum(II) bromide was studied. This reaction in liquid ammonia at −33.5° yields the hitherto unknown platinum(II) amide 2-ammonate which is thermally deammonated at 130–140° and completely decomposed to elemental platinum, ammonia and nitrogen, at 180–190°.

$$Pt(NH_3)_4Br_2 + 2KNH_2 \longrightarrow Pt(NH_2)_2 \cdot 2NH_3 + 2KBr + 2NH_3$$

$$Pt(NH_2)_2 \cdot 2NH_3 \longrightarrow Pt(NH_2)_2 + 2NH_3$$

$$3Pt(NH_2)_2 \longrightarrow 3Pt + 4NH_3 + N_2$$

Experimental

Materials.—With the exceptions noted below, all materials employed in this work were reagent grade chemicals or were prepared as described previously.[5]

Tetrammineplatinum(II) chloride was prepared as described by Keller[14] and converted to the corresponding bromide by an adaptation of the method of Reiset.[15] X-Ray diffraction data for this product are included in Table I.

Anal. Calcd. for $[Pt(NH_3)_4]Br_2$: Pt, 46.1; Br, 37.8. Found: Pt, 45.8; Br, 37.5.

TABLE I

X-RAY DIFFRACTION DATA FOR TETRAMMINEPLATINUM(II) BROMIDE AND *trans*-DIBROMODIAMMINEPLATINUM(II)[a]

$[Pt(NH_3)_4]Br_2$				$Pt(NH_3)_2Br_2$			
d, Å.	I/I_1	*d*, Å.	I/I_1	*d*, Å.	I/I_1	*d*, Å.	I/I_1
7.46	1.00	2.49	0.10	6.20	1.00	2.57	0.40
5.95	0.08	2.12	.12	5.00	0.70	2.52	.28
5.32	.08	2.08	.33	4.40	.22	2.25	.32
4.75	.07[b]	1.89	.22	4.11	.44	2.05	.55
3.77	.67	1.82	.15	3.57	.21	1.97	.15
3.37	.61	1.68	.09	3.42	.43	1.54	.15
2.66	.43			3.33	.70		

[a] These data were obtained using CuKα radiation, a Ni filter, a tube voltage of 35 kv. and a filament current of 15 ma. [b] Less intense lines not indexed.

trans-Dibromodiammineplatinum(II) was prepared by a modification of the method described by Keller,[14] *i.e.*, by heating tetrammineplatinum(II) bromide for 24 hr. at 150° in a stream of dry nitrogen.

Anal. Calcd. for $Pt(NH_3)_2Br_2$: Pt, 50.2; NH_3, 8.7. Found: Pt, 50.1; NH_3, 8.4.

That the product prepared in this manner is the *trans* isomer was confirmed by means of dipole moment measurements. Both pure dioxane and a solution of 0.108 g. of the *trans* isomer in 20.5 g. of dioxane both gave $\mu = 0.457$ Debye unit, which is to be compared with the previously determined value of 0.45 for pure dioxane.[16] X-Ray diffraction data for *trans*-$Pt(NH_3)_2Br_2$ are also given in Table I.

The Reduction of Tetrammineplatinum(II) Bromide with Potassium.[17]—Since preliminary experiments showed that the first end-point in this reaction is difficult to detect visually when the reaction is carried out on a large scale, the

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[6] G. W. Watt, G. R. Choppin and J. L. Hall, unpublished work.

[7] Products having somewhat higher decomposition temperatures were obtained from reactions involving the addition of a large excess of potassium. Although not yet identified, these products appear to be mixtures and contain potassium.

[8] L. Pauling, *Contrib. etude structure mol.*, Vol. commem. Victor Henri, 1947–1948, pp. 1–14; *C. A.*, **43**, 2830 (1949).

[9] E. G. Cox, *J. Chem. Soc.*, 1912 (1932); *cf.* D. P. Mellor, *Chem. Revs.*, **33**, 137 (1943).

[10] J. W. Eastes and W. M. Burgess, THIS JOURNAL, **64**, 1187 (1942).

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

[12] W. Hieber and C. Bartenstein, *Naturwissenschaften*, **13**, 300 (1952).

[13] The corresponding conversion in aqueous ammonia is well known; see M. Peyronne, *Ann.*, **12**, 193 (1844).

[14] R. N. Keller, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 250.

[15] J. Reiset, *Ann.*, **11**, 417 (1844).

[16] C. P. Smyth and W. S. Walls, THIS JOURNAL, **53**, 2115 (1931).

[17] For experimental procedures see: (a) G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949); (b) G. W. Watt and T. E. Moore, *ibid.*, **70**, 1197 (1948).

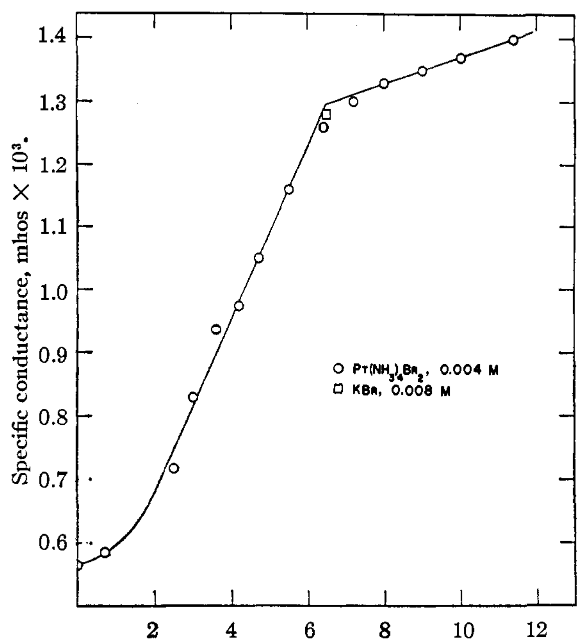

Fig. 1.—Conductimetric titration of tetrammineplatinum(II) bromide with potassium in liquid ammonia.

reaction ratio was established by means of conductimetric titrations. For example, a 0.004 *M* solution of $[Pt(NH_3)_4]Br_2$ in liquid ammonia was titrated with a 0.064 *M* solution of potassium. As shown in Fig. 1, the specific conductance changes progressively until two gram-atoms of potassium per mole of bromide have been added, and the conductance at this point is identical with that of a 0.008 *M* solution of potassium bromide in liquid ammonia.

In a typical reduction run, 1.14 g. of $[Pt(NH_3)_4]Br_2$ dissolved in 50 ml. of anhydrous liquid ammonia was titrated with a solution of 0.305 g. of potassium in 35 ml. of solution.[17a,18] Addition of potassium solution was continued until slightly in excess of two atomic equivalents had been added, whereupon the rate of consumption of potassium decreased sharply as evidenced by the rate of disappearance of the characteristic blue color. The reaction products consisted of a clear ammonia solution and a yellowish-white solid; insoluble gaseous products were not observed. The solid was separated by filtration and washed eight times with 100-ml. portions of ammonia; analysis of the combined filtrate and washings accounted for 98.5% of the bromide ion used as $[Pt(NH_3)_4]Br_2$. When the residual liquid ammonia was evaporated and the solid product was warmed to 0°, it appeared to undergo slow decomposition as evidenced by a slight darkening in color. A 0.251-g. sample of the product stable at 0° was decomposed completely by heating it to 100°. The decomposition products consisted of 0.214 g. of Pt and 49.4 cc. of ammonia; these data correspond to a ratio of 2.02 moles of NH_3/gram-atom of Pt.

Efforts to demonstrate higher ratios of ammonia to platinum were concerned largely with prevention of premature decomposition of the initial reduction product and with means for distinguishing between residual solvent ammonia and that combined with the platinum. These experiments included (a) attempts to remove unbound ammonia under reduced pressure at −70 to −33.5°, (b) displacement of residual solvent ammonia at −33.5° by dry oxygen-free helium, and (c) vapor pressure measurements over the temperature range −27 to 75°. Although some of these experiments gave NH_3 to Pt ratios higher than that indicated above, the results were not consistent. However, *in all cases, the only decomposition products were ammonia and platinum.*

The Conversion of *trans*-Dibromodiammineplatiuum(II) to Tetrammineplatinum(II) Bromide.—*trans*-Dibromodiammineplatinum(II) (0.067 g.) was exposed to a stream of dry gaseous ammonia over a period of 24 hr. at 25° during which the color of the solid changed from yellow to white. The weight of the final product was 0.073 g. as compared with 0.073 g. calculated on the assumption that the product was tetrammineplatinum(II) bromide. This product gave X-ray diffraction data essentially the same as those given in Table I for $[Pt(NH_3)_4]Br_2$.

Similarly, treatment of 0.205 g. of *trans*-dibromodiammineplatinum(II) with 35 ml. of anhydrous liquid ammonia at −33.5° resulted in a change from a yellow to a colorless solution. The white solid product remaining after evaporation of the solvent gave the X-ray diffraction pattern characteristic of $[Pt(NH_3)_4]Br_2$ (Table I).

The Action of Potassium Amide on Tetrammineplatinum(II) Bromide.—A solution of 1.103 g. of tetrammineplatinum(II) bromide in 50 ml. of liquid ammonia was treated with the potassium amide equivalent to 0.305 g. of potassium in 36 ml. of ammonia. The colorless supernatant solution was separated and the very voluminous white precipitate was washed six times with 30-ml. portions of liquid ammonia. Analysis of the residue from the combined supernatant solution and washings accounted for 98.5% of the bromide ion introduced initially as $[Pt(NH_3)_4]Br_2$.

A 0.5393-g. sample of the white solid product was placed in a Pyrex bulb, attached to a Toepler pump, evacuated at 25°, and thereafter the temperature was raised slowly. Over the range 130 to 140°, 0.0660 g. of ammonia was evolved; this is a weight loss of 12.3% as compared with a calculated value of 13.1% corresponding to the loss of two moles of ammonia/mole of platinum(II) amide 2-ammonate. At 185–190°, both ammonia and nitrogen were liberated. The *total* thermal decomposition products consisted of 0.4017 g. of platinum, 16.4 cc. of nitrogen and 154.1 cc. of ammonia, or 74.4, 3.8 and 21.8%, respectively. The corresponding values calculated on the assumption of complete thermal decomposition of $Pt(NH_2)_2{\cdot}2NH_3$ to Pt, N_2 and NH_3 are 74.6, 3.6 and 21.7%, respectively.

The Catalytic Activity of Platinum.—The activity of platinum from the low temperature decomposition of the ammine of platinum(0) as a catalyst for the hydrogenation of allyl alcohol was compared with that of a conventional platinum catalyst prepared by the method of Adams, Voorhees and Shriner.[19] The conditions and methods employed were the same as those described previously[5]; the data are given in Fig. 2.

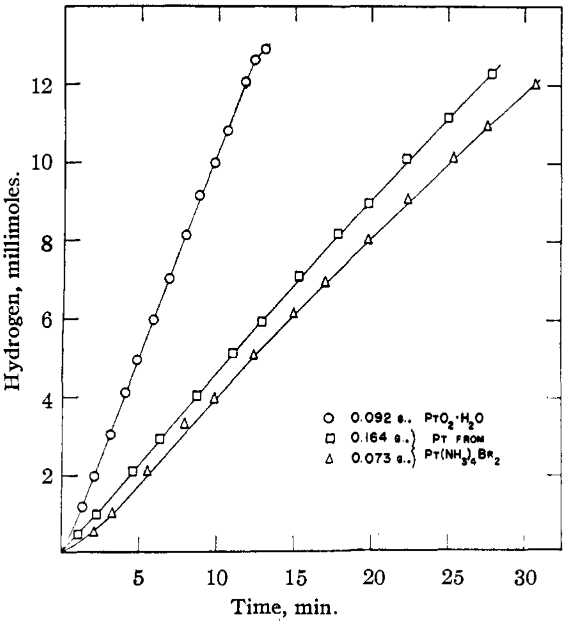

Fig. 2.—Hydrogenation of allyl alcohol over platinum catalysts.

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[18] Substantially identical results were obtained when solid potassium[17b] was added to the bromide, or when a solution of the bromide was added to a solution of potassium.

[19] R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1928, p. 92.