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Thermal Decomposition of Rhodium, Iridium, and Ruthenium Chlorides

A. E. NEWKIRK AND D. W. McKEE

From the Research and Development Center, General Electric Company, Schenectady, New York 12301

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The decomposition of rhodium, iridium, and ruthenium chloride hydrates in air and in hydrogen have been studied by means of thermogravimetric analysis; additional studies have been made of their reduction when dispersed on low- and high-area substrates. Under the conditions used, reduction to metal is complete at 105°, 190°, and ~350° for the Rh, Ir, and Ru salts, respectively. In air, dechlorination and oxidation are complete at 890°, 680°, and ~440°, respectively. Boron carbide, a low-area substrate, appears to exert little influence on the reduction temperature of the rhodium salt, whereas with alumina, a high-area support, desorption of decomposition products may be the cause for the slower rate of weight loss observed with all three salts.

INTRODUCTION

The decomposition and reduction of rhodium, iridium, and ruthenium chloride hydrates, both alone and on substrates, have been investigated by means of thermogravimetric analysis in order to develop information useful in the preparation of metal catalysts. For many catalytic purposes it is necessary to disperse a Group VIII metal on an inert substrate so as to increase the effective area of the metal phase and reduce the sintering that generally occurs with unsupported metal powders. A subject of considerable current interest is the relation between catalytic activity and the state of subdivision of the metal (*1*) and conflicting conclusions have been reached concerning the dependence of specific activity and metal crystallite size (*2*).

Metals of the platinum group are usually deposited on a support by impregnation with a suitable salt solution, often a halide, and subsequent reduction to the metal. However, in order to obtain optimum activity in such a supported catalyst it is necessary to choose a reduction temperature which is high enough to ensure complete reduction of the salt to the metallic state and low enough to avoid excessive sintering of the metal during the reduction step. In spite of this requirement reduction procedures for impregnated catalysts are often chosen arbitrarily and the resulting catalysts often vary widely in metal crystallite size and intrinsic catalytic activity.

Although the decomposition temperatures of platinum chloride in air and in hydrogen have been studied in some detail (*3*), little information is available on the behavior of the halides of rhodium, iridium, and ruthenium. Catalysts containing these metals are attracting considerable interest in fuel cell electrocatalysis (*4*) and in selective hydrogenation reactions (*5*). For this reason and also because of the discrepancies that exist in the published literature, we have studied the decomposition of the chlorides of rhodium, iridium, and ruthenium in some detail by means of thermogravimetric analysis.

EXPERIMENTAL

The experiments were carried out in a Chevenard thermobalance model TH-59. The furnace was fitted with a silica sheath so that experiments could be carried out in flowing gas, and the furnace temperature was measured just above the sample. Samples were contained in a quartz dish 15 mm in diameter and 4 mm deep. Gas flow rates were as follows: hydrogen, 250 ml/min; air, 275 ml/min. All thermograms were corrected for apparent weight gain. Products were characterized only by comparison of calculated and observed weight changes.

The salts were obtained from Engelhard Industries Inc. The rhodium(III) chloride hydrate was reported to have a rhodium content of 39.80%, which corresponds to $RhCl_3 \cdot 2.74\ H_2O$. The iridium(III) chloride hydrate was reported to have an iridium content of 54.52% which corresponds to $IrCl_3 \cdot 3H_2O$. The hydrated ruthenium chloride was reported to have a ruthenium content of 40.16%, which corresponds to $RuCl_3 \cdot 2.46\ H_2O$.

Results and Discussion

A. Rhodium Chloride

The reduction of $RhCl_3$ by hydrogen has recently been studied by Ivashentsev and Timonova (*6*) who observed that hydrogen chloride from the reaction

$$2\ RhCl_3 + 3\ H_2 = 2\ Rh + 6\ HCl$$

was first detectable at 120°C. Differential thermal analysis resulted in an exothermic peak beginning at 145°C and having a maximum at 205°C. Confirmation that the product was metallic rhodium was said to have been obtained by X-ray diffraction and thermogravimetric analysis, although the TGA curve was not given. They suggest that 175°C is a practical temperature for the reduction of $RhCl_3$ by hydrogen.

The behavior of $RhCl_3 \cdot xH_2O$ when heated in hydrogen has not been studied and the reports of its decomposition when heated in air are conflicting. Thus Gmelin (*7*) contains references both to reports that $RhCl_3 \cdot xH_2O$ can be heated to a red heat with the formation of anhydrous $RhCl_3$ and, to the contrary, that decomposition begins at 100°C to form Rh_2O_3 and HCl. The latter claim has also been made recently by Anderson and Basolo (*8*). However, Ivashentsev and Timonova (*6*), in a differential thermal analysis study, observed that the hydrate $RhCl_3 \cdot 4.86\ H_2O$ decomposed endothermically in flowing air at 105–140°C (range is initial temperature to peak temperature), to

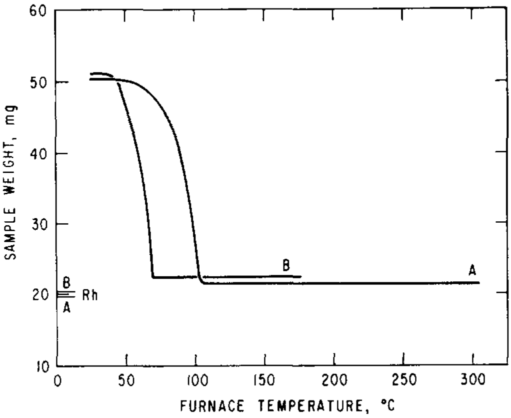

Fig. 1. Thermograms for $RhCl_3 \cdot 2.74\ H_2O$ in flowing hydrogen: A, heating rate 150°/hr; B, heating rate 25°/hr.

yield the anhydrous salt with a correct weight loss of 2.3%. On further heating the exothermic reaction

$$2\ RhCl_3 + 3/2\ O_2 = Rh_2O_3 + Cl_2$$

occurred from 440° to 500°C and the formation of Rh_2O_3 was confirmed by X-ray diffraction and thermogravimetric analysis. Finally at 940–970°C the Rh_2O_3 decomposed to Rh_2O and O_2.

i. Reduction by Hydrogen

Rhodium(III) chloride hydrate, sample weight 50.1 mg, heated at a rate of 150°C/hr in flowing hydrogen gave the thermogram shown in Fig. 1.A. Weight loss was first detected at 35°C and increased rapidly in a single step to about 105°C. The weight was constant to 300°C at 21.5 mg, but increased slightly above this temperature, as shown in Fig. 6,A. The residue was cooled in hydrogen and reweighed in air on an analytical balance. Found: 19.7 mg; calcd. for Rh: 19.9 mg.

A second portion weighing 51.1 mg was heated at 25°C/hr to 172°C as shown in Fig. 1,B and then rapidly to 415°C. The initial weight loss temperature, 35°C, was the same as for the more rapidly heated portion, but the extent of decomposition at any temperature above this was greater, as expected. Above 70° residue weight was constant at 22.2 mg. After cooling in hydrogen and reweighing in air the sample

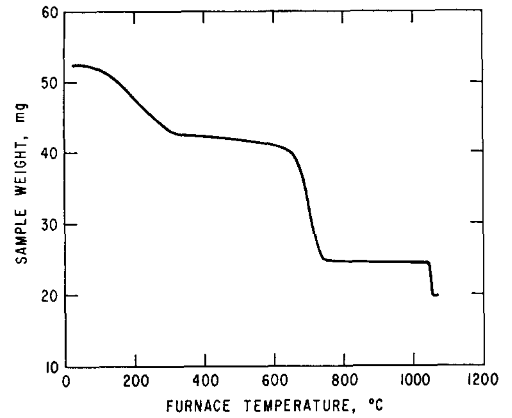

FIG. 2. Thermogram for $RhCl_3 \cdot 2.74\ H_2O$ in flowing air at a heating rate of 150°/hr.

was analyzed. Found: 20.1 mg; calcd. for Rh: 20.3 mg.

These results are in good agreement with those of Ivashentsev and Timonova (*6*) and confirm their suggestion that 175°C is a practical temperature for the reduction of $RhCl_3$ by hydrogen. Lower temperatures could be used if desirable.

ii. Oxidation in Air

A 52.4-mg sample of rhodium(III) chloride hydrate when heated in flowing air gave the thermogram shown in Fig. 2. Weight loss was first detected at 50°C. The first plateau, from about 340° to 505°C, is not strictly horizontal although the weight loss corresponds closely to the calculated loss of water. (Calculated for $RhCl_3 \cdot 2.74\ H_2O = RhCl_3$: 10.0 mg. Observed loss: at 340°C, 9.8 mg; at 505°C, 10.4 mg.) The second plateau appears to start at about 755°C but is horizontal only from 890° to 1040°C. The total weight loss corresponds to the reaction

$$2\ RhCl_3 \cdot 2.74\ H_2O + 1.5\ O_2 = Rh_2O_3 + 2.74\ H_2O + 3Cl_2$$

(Calculated loss: 26.7 mg. Observed loss: at 755°C, 27.8 mg; at 890°C, 28.1 mg; at 1040°C, 28.1 mg.) Better agreement with experiment can be obtained with the reaction

$$RhCl_3 \cdot 2.74\ H_2O + 0.5\ O_2 = RhO + 2.74\ H_2O + 1.5\ Cl_2$$

(Calculated loss: 28.3 mg.) However, the next stage weight loss from 1040° to 1060° corresponds more closely to the decomposition

$$2\ Rh_2O_3 = 4\ Rh + 3\ O_2$$

than to

$$2\ RhO = 2\ Rh + O_2$$

Sample weight at 1040°C = 24.18 mg. (Observed loss: 4.5 mg. Calculated loss for Rh_2O_3: 4.3 mg; for RhO: 3.4 mg.) On cooling the sample shows a rapid weight gain of 0.64 mg between 1015° and 995°C. The calculated gain for a reaction giving the smallest gain

$$2\ Rh + 0.5\ O_2 = Rh_2O$$

is 0.77 mg for 19.8 mg of Rh, the observed sample weight at 1060°C.

These results indicate, in rough agreement with the work of Ivashentev and Timonova (*6*), that rhodium(III) chloride hydrate may be dehydrated to $RhCl_3$ in air in the temperature range 50° to 340°C without appreciable loss of chlorine, and that at temperatures above 505°C, the anhydrous chloride reacts with atmospheric oxygen to form the oxide Rh_2O_3. The selection of Rh_2O_3 as the stable phase for the plateau from 755° to 1040° is also in agreement with the work of Dollimore *et al.* (*10*), who observed that the complex $[Rh\ bipy_2Cl_2]Cl$ reacted in air in the temperature range 400–600°C to form Rh_2O_3 which was stable to 1000°C. In contrast to the work of Ivashentev and Timonova (*6*), Rh_2O_3 appears to be stable in air up to 1040°C, above which it decomposes rapidly to metallic rhodium and not to Rh_2O. This conclusion is in agreement with the results of Schmahl and Minzl (*11*), from which a decomposition temperature of 1032°C in air can be calculated for Rh_2O_3. These authors found Rh as the decomposition product and did not detect Rh_2O or RhO as stable phases. The weight gain on cooling from 1060°C also agrees with the work of Frier and Jaffee (*12*), who observed that rhodium gained weight in flowing air at 1000°C. However, owing to the rapid cooling rate, no significance should be attached to the magnitude of the gain.

B. Iridium Chloride

Little information is available in the literature on the reduction of $IrCl_3$ in hydrogen, although supported iridium catalysts have frequently been prepared by heating substrates impregnated with the salt at 200°C and above (*13*). More data can be found on the oxidation of $IrCl_3$ and the thermal stability of the iridium oxides but the results are often confusing. According to Lunde (*14*) $IrCl_3$ is decomposed to IrO_2 on heating in oxygen for 1 hr at 800°C, although Cordfunke and Meyer (*15*) report that above 800°C the dissociation of IrO_2 gives rise to a nonstoichiometric oxide, IrO_{2-x}, which progressively loses oxygen,

$$IrO_{2-x}(s) = Ir(s) + \tfrac{1}{2}(2 - x)O_2(g)$$

the value of x depending on temperature. In addition the volatile oxide IrO_3 is believed to be formed at higher temperatures, together with IrO_2Cl when chlorine is present (*16*). However, according to the thermogravimetric studies of Duval *et al.* (*17*), iridium 2-mercaptobenzothiozole when heated in air gave metallic iridium at 520°C and the metal weight remained constant to 980°C.

i. Reduction by Hydrogen

The reduction of a 79.0-mg sample of $IrCl_3{\cdot}3H_2O$ in flowing hydrogen gave the thermogram shown in Fig. 3,A. The weight loss was first detected at a temperature of 50°C and was complete at 190°C. The sample weight was constant, within the random error of the instrument, up to 770°C, the maximum temperature used. After cooling in hydrogen, and reweighing in air on an analytical balance the loss was as follows: obs., 35.8 mg; calculated, 35.9 mg for a residue of Ir. Complete reduction could probably be achieved isothermally at a temperature of 150°C or lower.

ii. Oxidation in Air

A sample of $IrCl_3{\cdot}3H_2O$ weighing 78.8 mg when heated in flowing air gave the thermogram shown in Fig. 3,B. The weight loss was first detected at 50°C and continued slowly to a sloping plateau with a midpoint at 350°C. At this temperature the residue weight was 68.3 mg compared with 67.0 mg calculated for anhydrous $IrCl_3$. After further loss in weight a sloping plateau was reached at 680°C. The residue weight at 695°C was 49.2 mg compared with 50.7 mg calculated for IrO_2. A slow weight loss of 0.9 mg occurred between 680° and 915°C, a faster loss of 0.9 mg to 1025°C, and a very rapid loss above this temperature to a residue weight of 39.4 mg at 1070°C. On cooling, the residue weight on an analytical balance was 44.4 mg.

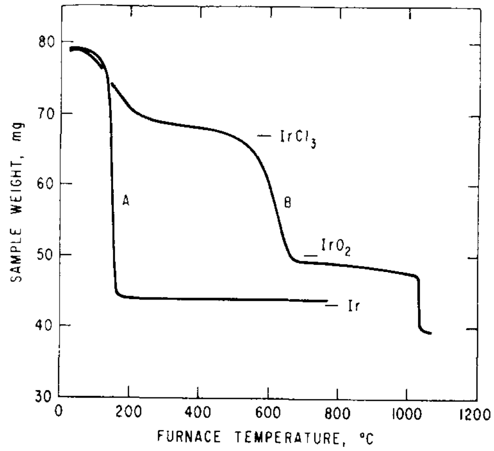

FIG. 3. Thermograms for $IrCl_3 \cdot 3H_2O$ at a heating rate of 150°/hr: A, in flowing H_2; B, in flowing air.

These results may be interpreted as indicating that $IrCl_3{\cdot}3H_2O$ decomposes on heating to lose water and chlorine in overlapping stages, as shown by a sloping plateau centered at about 350°C. The intermediate or intermediates then oxidize to the start of a second sloping plateau at 680°C, corresponding approximately to IrO_2. A slow weight loss occurs on further heating to 1025°C, above which a very rapid weight loss occurs, probably due to the dissociation of IrO_2 to Ir and oxygen. If the sample at 1025°C is assumed to be IrO_2 the calculated weight loss is 6.8 mg for the 47.4-mg sample compared to the observed loss from 1025° to 1040°C of 7.6 mg. It was noted on cooling that the support rod was coated on its lower part with a dark film, which would

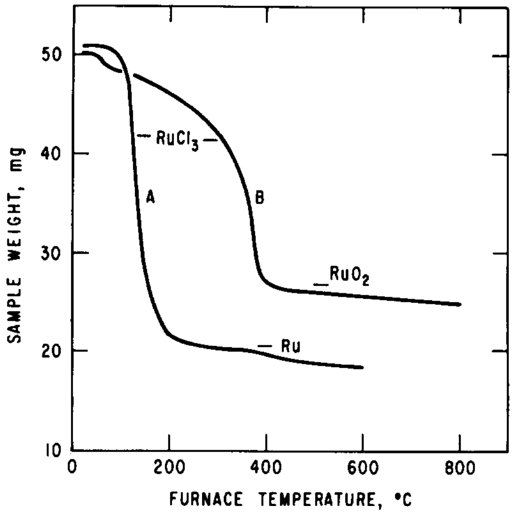

FIG. 4. Thermograms for $RuCl_3 \cdot 2.46\ H_2O$ at a heating rate of 150°/hr: A, in flowing H_2; B, in flowing air.

be expected if an iridium oxide was vaporizing in the temperature range above 680°C.

C. Ruthenium Chloride

Interpretation of the properties of ruthenium chloride is complicated by the fact that this salt is unusually ill-defined. Although two distinct forms of $RuCl_3$ have been isolated (*18*), commercial ruthenium chloride is apparently a water-soluble mixture of aquochloro complexes of polynuclear Ru(IV), which on heating in chlorine gives a residue containing Ru_2OCl_6 (*19*). Early claims by Aoyama (*20*) that oxidation of ruthenium metal obtained by reduction of ruthenium salts yielded only Ru_2O_3 at 600°C were contested by Lunde (*14*) and more recently by Bell and Tagami (*21*), who found that RuO_2 is the only stable solid species formed by heating ruthenium in oxygen. Above 760°C both Ru metal and RuO_2 can form volatile RuO_3 when heated in oxygen.

i. Reduction by Hydrogen

Thermograms for hydrated ruthenium chloride are shown in Fig. 4. Weight loss of a 50.8-mg sample in hydrogen began slightly above 60°C and occurred in a single major step between this temperature and 350°C. At higher temperatures the rate of weight loss increased slightly then decreased again, although the sample was still losing weight slowly at 600°C, the maximum temperature attained.

ii. Oxidation in Air

Weight loss of a 50.2-mg sample in air began slightly above room temperature. The thermogram showed a bend at 80°C but above this temperature the weight loss continued in a single step to approximately 440°C. From 440° to 800°C there was a uniform small loss.

Fiducial marks on the two curves indicate the calculated weights for possible intermediates and products. There is no indication on either curve for anhydrous $RuCl_3$. The product in hydrogen had an appropriate weight for elemental ruthenium and in air an appropriate weight for ruthenium(IV) oxide. The continuing weight loss in air might be due to volatile RuO_3, but it is not obvious why there should be a continuing weight loss in hydrogen. It seems more likely that the starting compound was a mixture of Ru aquochloro complexes as suggested by Fletcher *et al.* (*19*).

D. Reduction of Chlorides Dispersed On Substrates

Since the metals of the platinum group are generally employed as catalysts in supported form, attempts were made to determine whether the presence of an inert substrate had an appreciable effect on the decomposition behavior of the metal halides. Boron carbide (surface area 11 m^2/g) and γ-alumina (140 m^2/g) were chosen as being representative of low- and high-area substrates, respectively. Boron carbide has also been shown to be a satisfactory support material in fuel cell electrocatalysis (*9*).

Boron carbide powder (Norton Co., 400 mesh) was impregnated with an aqueous solution of rhodium chloride and the mixture evaporated to dryness under a heat lamp. The product was ground and sieved through a 400-mesh nylon screen. A portion of this material, weighing 150.5 mg, was heated to 400°C in flowing hydrogen in the thermo-

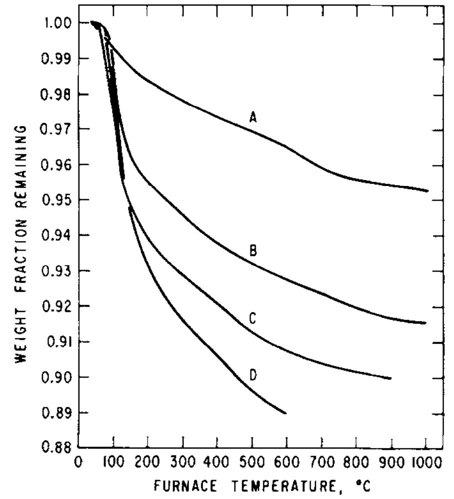

FIG. 5. Thermograms in flowing hydrogen at a heating rate of 150°/hr: A, alumina, 188.5 mg; B, $IrCl_3$-alumina, 199.9 mg; C, $RhCl_3$-alumina, 186.0 mg; D $RuCl_3$-alumina, 170.6 mg.

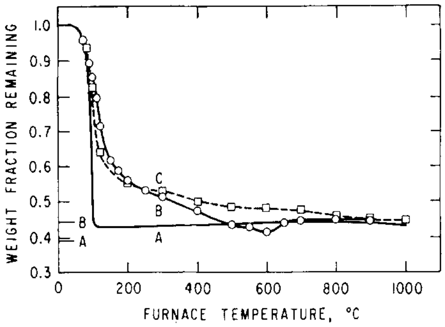

FIG. 6. Comparison thermograms: A, reduction of $RhCl_3 \cdot 2.74\ H_2O$; B, reduction of $RhCl_3 \cdot 1.21\ H_2O$ on alumina, corrected for alumina; C, weight loss of aqueous hydrogen chloride on alumina, corrected for alumina.

balance. The resulting thermogram was similar to that shown in Fig. 1,A but displaced slightly to higher temperature. The observed weight losses were 28.8 mg at 135°C and 30.9 mg at 400°C. Although the composition of the starting material was indefinite after drying, it appears that the boron carbide support did not have any major effect on the decomposition of the salt.

γ-Alumina (J. T. Baker Co.) was dried at 300°C for 3 hr, treated with an aqueous solution of the metal halide in an amount equivalent to 5% metal content for metal plus alumina, (the blank was treated with water) evaporated to dryness under a heat lamp, crushed, and stored in a desiccator over Drierite. Separate thermograms were obtained for these powders and for the alumina.

The results are shown in Fig. 5. A weight loss for alumina was detected as low as 45°C, and continued smoothly up to 1000°C, at which temperature the experiment was stopped. The thermograms were measured and corrected at numerous points up to 300° and at 100° intervals thereafter. The treated samples showed initial weight losses at 50° to 80°C and very rapid losses thereafter due to reduction of the halides. If it is assumed that the residue is only metal and slightly hydrated alumina and that, for purposes of comparison, the water content of the initial alumina is equal to the weight loss between its initial and final temperature, the initial composition of the samples can be calculated. This yields: $RhCl_3 \cdot 1.21\ H_2O$, 0.106 weight fraction; alumina, 0.894 weight fraction, from the results at 900°C; $IrCl_3 \cdot 2.12\ H_2O$, 0.0847 weight fraction; alumina, 0.915_3 weight fraction, from the results at 1000°C. The composition of the ruthenium salt was not calculated because even when run alone it did not yield readily interpretable results. (See Section C.)

From the thermograms of the salts on alumina and that of alumina alone it is possible to calculate thermograms for the salts and thus to compare their behavior

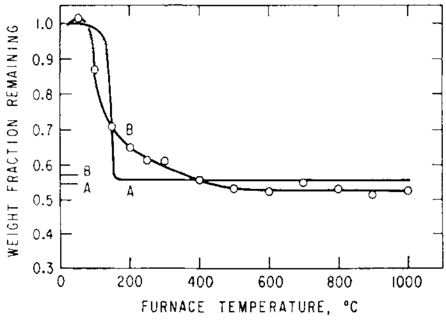

FIG. 7. Comparison thermograms: A reduction of $IrCl_3 \cdot 3H_2O$; B, reduction of $IrCl_3 \cdot 2.12\ H_2O$ on alumina, corrected for alumina.

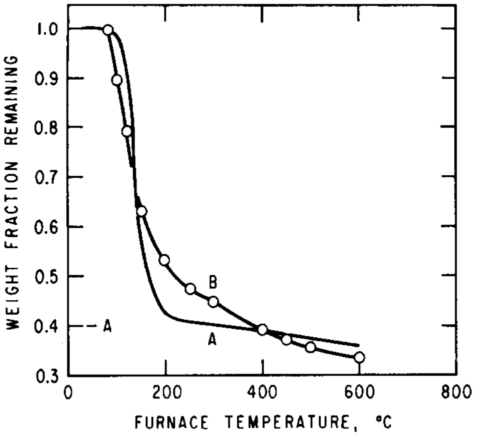

FIG. 8. Comparison thermograms: A, reduction of $RuCl_3 \cdot 2.46\ H_2O$; B, reduction of $RuCl_3 \cdot xH_2O$ on alumina, corrected for alumina.

when reduced alone and when reduced in the presence of alumina. For this purpose the following equation may be used:

$$(WFR)_{mix} = (WFR)_A(WF)_A + (WFR)_C(WF)_C$$

where, WFR is the weight fraction remaining at a given temperature; WF, the weight fraction in the sample; and mix indicates mixture of alumina plus metal chloride hydrate; A, alumina; and C, metal chloride hydrate. Thermograms for the mix and for alumina provide all information needed to calculate $(WFR)_C$.

The results are shown in Figs. 6, 7, and 8 in which curve A in each case is that of the metal chloride hydrate decomposed separately and curve B is the curve for the hydrate calculated from the thermogram obtained from the mixture. In each case a fiducial point is given on the left-hand axis for the metal content, and the points at which the calculations were made for the curves labeled B are indicated. Not too much significance can be placed on the absolute magnitude of the final level of the curves labeled B because they represent small differences between large numbers. Thus, the weight of metal halide was only 19.7 mg in Fig. 6 and 16.9 mg in Fig. 7. The minimum in curve 6,B and the spread of the points on the final plateau in curve 7,B are, therefore, probably due to experimental error.

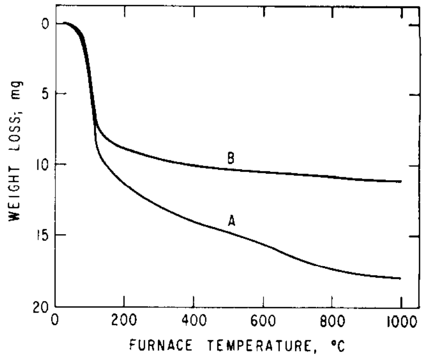

FIG. 9. Comparison thermograms: A, alumina, 146.6 mg and aqueous hydrogen chloride, 11.1 mg; B, curve A corrected for weight loss of alumina.

The most important result indicated in Figs. 6 and 7 is that attainment of the maximum weight loss requires a higher temperature when the halide is dispersed on alumina than when it is unsupported. This may be due to (a) adsorption of water by alumina; (b) adsorption of HCl by alumina; (c) slower reaction rates of the halides in pores of alumina than in an open dish. Several simple experiments were carried out to test these possibilities. A portion of the alumina weighing 191.6 mg was placed in a shallow quartz dish and 157.0 mg of water was added. The sample was placed in a covered, but not sealed, Petri dish. About 18 hr later only 43 mg of water remained, and after 5 days, only 2 mg of water remained. A similar experiment was performed in the thermobalance in an atmosphere of flowing hydrogen. More than 95% of the water was removed in the first hour. When concentrated HCl was used, only 75% of it was lost in the first hour and even after 3 hr the weight loss was only 80%.

The second experiment was repeated with a fresh sample of alumina weighing 146.6 mg. To this was added 124.7 mg of reagent grade hydrochloric acid (Fisher Scientific Co.). The sample was treated in flowing hydrogen for 210 min, at which time the rate of weight loss was nearly zero. After storage overnight, the sample was heated to 1000° in the thermobalance at a heating rate of 150°/hr. The results are shown in Fig. 9. The interesting feature of this experiment, as shown by the derived curve B of Fig. 9, is that all the added aqueous hydrogen chloride was not removed until the sample had been heated to 900°C. Curve B was normalized so that the total loss was equal to 0.45 weight fraction remaining and the results are plotted as a dashed line in Fig. 6. The close correspondence between this curve and that of rhodium chloride hydrate on alumina would seem to indicate, but not prove, that the difference between the thermograms for rhodium chloride hydrate alone and rhodium chloride hydrate on alumina is due simply to the adsorption by the alumina of the hydrogen chloride produced in the reduction.

SUMMARY

The results of this study indicate that, for catalytic purposes, reduction temperatures in the range 150–200°C are sufficient to reduce the chlorides of rhodium and iridium, and perhaps ruthenium to the elemental metals. Higher temperatures are unnecessary and may result in loss of metal surface area by sintering. The limited data available on the reduction of metal chlorides supported on low-area substrates do not indicate that the substrate exerts an important influence on the reduction temperature of the salt. However, it is likely that with supports of high area, the isolated crystallites of halide may decompose at appreciably different temperatures from the bulk crystals and the products of the decomposition may be retained on the adsorbent surface. This point would be worthy of further investigation with substrates of different types. Although platinum dioxide, PtO_2, is known to decompose to metallic platinum above 500°C in oxygen it appears very unlikely that metallic phases could be obtained by calcining the chlorides of rhodium, iridium, and ruthenium in air below 1000°C. Above this temperature loss of metal occurs by formation of volatile oxides.

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