Thermolysis of ternary ammonium chlorides of rhenium and the noble metals

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(Received December 6, 1990)

Abstract

Thermal decomposition of the ammonium hexachlorometalates $(NH_4)_2[MCl_6] (M \equiv Pd, Re, Os, Ir, Pt)$, $(NH_4)_3[RhCl_6] \cdot H_2O (NH_4)_4[Ru_2Cl_{10}O]$ was investigated by means of thermogravimetry, differential thermal analysis, mass spectrometry and X-ray diffraction dependent upon temperature. All ammonium compounds produce, finally, finely divided metal powders. Nitrogen and hydrogen chloride, are released as gases attesting to the internal redox reaction $M^{4+}(M^{3+}) + N^{3-} \rightarrow N_2^{\pm 0} + M^{\pm 0}$ which takes place in all cases at temperatures between 300 and 450 °C depending upon the heating rates and the element M. For $M \equiv Rh$ and Pd, stable intermediates could be detected, namely $(NH_4)_2[Rh(NH_3)Cl_5]$ and $(NH_4)_2[PdCl_4]$.

1. Introduction

Rhenium in its oxidation state +4 and the noble metals—palladium, platinum, osmium and iridium—form ammonium hexachlorometalates $(NH_4)_2[MCl_6]$. They are easy to prepare from aqueous solutions and have, therefore, been known for a long time— $(NH_4)_2[PtCl_6]$ since 1817. Ruthenium and rhodium are exceptions in that they form complex ammonium chlorides with the compositions $(NH_4)_4[Ru_2Cl_{10}O]$ and $(NH_4)_3[RhCl_6] \cdot H_2O$ under identical experimental conditions. All these chlorides may be easily reduced to the metals with hydrogen at slightly elevated temperatures. The metals are thereby obtained as finely divided powders and may be used for catalytic purposes. The metals are also produced by thermal decomposition of the ammonium chlorometalates alone. However, the mechanism of this thermal decomposition process remained unclear although first reports date back as far as 1826 [1]. It was usually suggested that, for example, $(NH_4)_2[PtCl_6]$ would decompose to the binary components, NH_4Cl and $PtCl_4$, first and then the $PtCl_4$ would decompose to platinum metal and chlorine.

A re-investigation of the thermal decomposition of these complex ammonium chlorides has now been undertaken.

2. Experimental details

 $(NH_4)_2[ReCl_6]$ was synthesized from NH_4ReO_4 by reduction with hypophosphoric acid in hydrochloric acid solution with the addition of NH_4Cl [2].

 $(NH_4)_2[MCl_6]$ -type chlorides with $M \equiv Os$, Ir, Pd and Pt were used as supplied by Degussa (Hanau); $(NH_4)_3[RhCl_6] \cdot H_2O$ (Degussa) was recrystallized from hydrochloric acid. $(NH_4)_4[Ru_2Cl_{10}O]$ was obtained from a solution of RuCl₃ · 6H₂O and NH₄Cl in an ambient atmosphere.

All educts were checked for purity by X-ray powder diffraction (the Guinier method). No lines other than those expected for the K₂PtCl₆-type structure of $(NH_4)_2[MCl_6]$ (M=Re, Os, Ir, Pt, Pd) were observed, for details see ref. 3. $(NH_4)_3[RhCl_6] \cdot H_2O$ crystallizes with the orthorhombic crystal system: a = 1218.65(7); b = 701.63(3); c = 1415.87(4) pm; and the space group is *Pnma*. This structure has been refined from single crystal data. The atomic parameters are essentially identical to those previously determined [4]. $(NH_4)_4[Ru_2Cl_{10}O]$ is isostructural to K₄[Ru₂Cl₁₀O] [5]; the lattice constants have been determined from X-ray powder data: a = 726.56(9); c = 1716.7(3) pm; and the space group is *I4/mmm*.

The thermal decomposition was followed visually in a glass furnace, by hightemperature X-ray powder diffraction (Simon camera [6], FR 553, Enraf-Nonius), by simultaneous thermogravimetry (TG), differential thermal analysis (DTA) and, partly, also by mass spectrometry (MS) (Netzsch STA429/Balzers QMS 511).

3. Results and discussion

At temperatures between 300 and 450 °C, the thermal decomposition of the ammonium hexachlorometalates of the noble metals and rhenium, $(NH_4)_2[MCl_6]$ $(M \equiv Pd, Re, Os, Ir, Pt)$, of $(NH_4)_4[Ru_2Cl_{10}O]$ and $(NH_4)_3[RhCl_6]$ begins. In all cases the final products are the metals in form of finely divided powders if sufficient care has been taken to keep oxygen (or water) from the metal *in statu nascendi*. Otherwise, oxides or oxychlorides are formed, for example ReOCl₄, OsO₄, IrO₂, RuO₂ and Rh₂O₃.

Table 1 gives a summary of the decomposition temperatures that were obtained by simultaneous thermogravimetry and differential thermal analysis experiments at heating rates of 5 K min⁻¹. In some cases, *i.e.* M = Rh, Pd, Pt, simultaneous mass spectrometry of the released gases of the masses 28, 35 and 36 was undertaken. Figure 1 shows the results for $(NH_4)_2[PtCl_6]$ and $(NH_4)_3[RhCl_6] \cdot H_2O$. Additionally, in all cases, high-temperature X-ray patterns were recorded making use of the Guinier–Simon technique with heating rates of 10 K h⁻¹ with simultaneous film support. There was no evidence for any other intermediate products than those reported in Table 1.

Therefore, intermediates could be detected only in the cases of M = Pd and Rh.

In the first case, $(NH_4)_2[PdCl_6]$ apparently releases chlorine between 250 and 280 °C yielding $(NH_4)_2[PdCl_4]$ [7] and shortly thereafter, the "decomposition" to palladium metal takes place. This result is in contrast to a previous investigation where decomposition to the binary components, *i.e.* $2NH_4Cl+PdCl_2$, was suggested [8].

TABLE 1

Decomposition temperatures (from TG/DTA/MS experiments) and solid products (from X-ray diffraction) of the thermal decomposition of complex ammonium chlorides of rhenium and the noble metals

Educt	Temperature (°C)	Product(s)	
(NH ₄) ₃ [RhCl ₆]·H ₂ O	60-160 320-380 410-440	(NH ₄) ₃ [RhCl ₆] (NH ₄) ₂ [RhCl ₅ (NH ₃)] Rh	
$(NH_4)_2[PdCl_6]$	250-280 310-370	$(\mathbf{NH}_4)_2[\mathbf{PdCl}_4]$ Pd	
$(NH_4)_4[Ru_2Cl_{10}O]$	340-360	Ru	
(NH ₄) ₂ [ReCl ₆]	420	Re	
$(NH_4)_2[OsCl_6]$	390	Os	
$(NH_4)_2[IrCl_6]$	455	Ir	
(NH ₄) ₂ [PtCl ₆]	370-410	Pt	

In the second, more interesting case, $(NH_4)_3[RhCl_6]$ releases 1 mol of HCl between 320 and 380 °C (TG/DTA/MS) yielding $(NH_4)_2[RhCl_5(NH_3)]$. This reaction gives an important hint at the mechanism of all these so-called thermal decomposition reactions. As $(NH_4)_2[RhCl_5(NH_3)]$ could be detected as a stable intermediate, see also [9], and analysed by X-ray diffraction (isotypic with $K_2[RhCl_5(H_2O)][10]$) and infrared spectroscopy, it becomes clear that a ligand substitution, chloride with ammonia, must be the initial step of the decomposition process. The second step may then be interpreted as an internal redox reaction where the ammonia ligand (*i.e.* N³⁻) reduces the central rhodium cation (Rh³⁺). These reactions may be formulated as follows.

$$(NH_4)_3[RhCl_6] = (NH_4)_2[RhCl_5(NH_3)] + HCl_5(NH_3)$$

 $(NH_4)_2[RhCl_5(NH_3)] = Rh + \frac{1}{2}N_2 + 3HCl + 2NH_4Cl$

The TG/MS spectra of Fig. 1 show clearly that there are two distinct steps in the TG curve and in the curves for masses 35 and 36 (HCl) but not for mass 28 (N₂) which exhibits only one sharp effect peaking at 385 °C. This is the same temperature at which the second HCl peak starts. The broadness of this peak attests to a slow release of HCl and, more importantly, to the slow transfer of HCl, especially through the decomposition of NH₄Cl, into the mass spectrometer. This may also be the reason why in several cases "after-peaks" are observed for masses 35 and 36, see Fig. 1 for $(NH_4)_2[PtCl_6]$.

It is interesting to note in this connection that in the case of $(NH_4)_2[PtCl_6]$ a shoulder is observed in the mass peaks for HCl and in the TG curve at the lower temperature side. This could be attributed to a ligand-substitution reaction similar



Fig. 1. Simultaneous thermogravimetry and mass spectrometry of the gases (masses: 28, 35 and 36) released during the "thermal decomposition" of (a) $(NH_4)_2[PtCl_6]$ and (b) $(NH_4)_3[RhCl_6] \cdot H_2O$.

to that previously detected and described, for example:

 $(NH_4)_2[PtCl_6] = [PtCl_2(NH_3)_2] + 4HCl$

This reaction could not be observed by X-ray diffraction which could simply mean that the following redox reaction is just too fast that the intermediate would be stable enough to be detectable on the Guinier time scale with a heating rate of 10 K h^{-1} . Therefore, only the total reaction can be formulated as follows.

 $3(NH_4)_2[MCl_6] = 3M + 2N_2 + 16HCl + 2NH_4Cl$ M = Re, Os, Ir, Pt

This does not necessarily reflect the mechanism of the "decomposition" reaction of the ternary chlorides $(NH_4)_2[MCl_6]$.

In conclusion, the results, as reported here, prove that the thermal decomposition of ammonium hexachlorometalates, $(NH_4)_2[MCl_6]$ ($M \equiv Pd$, Re, Os, Ir, Pt), of $(NH_4)_4[Ru_2Cl_{10}O]$ and $(NH_4)_3[RhCl_6]$ are not decompositions to the binary components, *e.g.* to NH_4Cl and $PtCl_4$, followed by the decomposition of the chloride to the metal and chlorine, *i.e.* by the reduction of Pt^{4+} by Cl^- . Although the decomposition of $PtCl_4$ is known it only occurs at 480 °C [11]. A redox reaction takes place instead between, for example, Pt^{4+} and nitrogen of the oxidation state -3. This "N³⁻" is certainly the ammonia ligand in the case of $(NH_4)_3[RhCl_6]$ where the intermediate $(NH_4)_2[RhCl_5(NH_3)]$ is observed. In the case of $(NH_4)_2[PtCl_6]$, however, if an intermediate like $(NH_4)[PtCl_5(NH_3)]$ or $[PtCl_2(NH_3)_2]$ were to occur, the redox reaction cannot be that simple because the number of exchangeable electrons does not fit. It seems possible that "N³⁻" of NH_4^+ could also be a reducing agent.

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft, Bonn, and by Degussa, Hanau. We are especially grateful to Netzsch, Selb, for the TG/DSC/MS measurements.

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